Ambient Air Measurements of Polycyclic Aromatic Hydrocarbons (PAH), Polychlorinated Dibenzo-*p*-Dioxins (PCDD) and Polychlorinated Dibenzofurans in Canada (1987-1997)

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Executive Summary

As a component of the National Air Pollution Surveillance (NAPS) network, the Analysis and Air Quality Division (AAQD), Environmental Protection, Environment Canada operates an ambient air measurement program for polycyclic aromatic hydrocarbons, polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). With the co-operation of provincial and municipal environment agencies and Environment Canada regional offices, samples have been collected at thirty-nine urban and rural monitoring sites across Canada. This reports summarizes available results for the period 1987 to 1997 (most data were collected between 1995 and 1997).

The category of compound known as PAH has received a good deal of attention over the last thirty years because some species of PAH are known human carcinogens. Because PAH result from the incomplete combustion of fossil fuels they are ubiquitous in the atmosphere. Based on an inventory of Canadian emissions of PAH for 1990 the primary anthropogenic sources of PAH are aluminum smelting, residential wood combustion, open air burning and diesel motor vehicles. Forest fires account for 46% of total emissions in the inventory, but their impact on average measured ambient PAH concentration is generally small. PAH appeared on the Canadian Environmental Protection Act (CEPA) priority substances list (PSL) and five species (benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene) were designated 'toxic' as defined in Section 11c (constituting a danger to human life or health) of the Act. Nine PAH (acenapthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene and naphthalene) were found to be toxic under Section 11a (having a harmful effect on the environment).

Numerous assessments of PCDD/PCDF have recognized that because of their toxicity to animals, their persistence and their ability to bio-accumulate, they represent a significant danger to human health and to the environment. Of the 210 possible PCDD/PCDF congeners, it is the 2,3,7,8 substituted PCDDs and PCDFs that are of most concern from a health and environmental effect perspective. Of these, the 2,3,7,8-TCDD isomer has been shown to be the most toxic to mammals. There is no intentional production or use of PCDD/PCDF. They are released into the environment as contaminants or by-products associated with the production or combustion of chlorinated organic substances. The recently released Federal Provincial Advisory Committee for the Canadian Environmental Protection Act (CEPA-FPAC) inventory for dioxins, furans and hexachlorobenzene shows that incineration accounted for ~60% of PCDD/PCDF emissions in 1990.

Data from approximately 2,200 daily PAH samples collected at 35 sites are available. For 1994-1997 data, mean PAH concentrations vary by more than three orders of magnitude from the rural-remote Jasper Park sites to the industrial influenced Jonquière site (the range of means is 0.9 to 801 ng/m^3 and the range of 90th percentile values is 4.8 to 2,650 ng/m^3). For the urban sites (with more than 10 sampling days of data) mean total PAH concentrations ranged from 10 to 65

ng/m³ with 90th percentile concentrations ranging from 14 to 115 ng/m³. In general, the larger population areas experienced the highest mean and 90th percentile PAH concentrations. The sites with industrial emission sources (or wood smoke in the case of the Whitehorse site) nearby recorded the highest mean and 90th percentile concentrations. The most abundant species were phenanthrene, fluoranthene, pyrene and benzo(b)&(k)&(j) fluoranthene with frequencies of detection ranging from 94 to 99.9%. In contrast the species with the lowest frequency of detection were 3-Me-cholanthrene and 7-Me-Benz(a)anthracene. Overall, vapor phase species account for most of the PAH mass with particulate phase species found in much lower concentrations.

For sites with the longest data records (Jonquière, Montréal, Toronto, Hamilton and Windsor) yearly variations in the sum of the CEPA toxic (health) PAH were determined. For Jonquière, median concentrations decreased substantially through the period with smaller decreases in 75th and 90th percentile values. The Hamilton site shows substantial year to year variation but the median concentration for 1996 was the same as for 1989. The Montreal site appears to be experiencing an upward trend whereas median concentrations at the Toronto site show a significant decline between 1994 and 1996.

Over 500 daily samples were collected for PCDD/PCDF analysis from 34 monitoring sites with 344 samples collected between 1994 and 1997. For many sites, however, only 2 or 3 days of data are available. The only sites with long data records are Windsor-University Ave. (1989 to 1995), Windsor-College and Prince (1990-1997) and Walpole Island (1989-1995). Overall, mean TEQ concentrations (using 0.5-DL substitution) ranged from 105 fg/m³ at the Toronto site to 10 fg/m³ at St. Andrews, N.B. For sites with more than ten sampling days, ninetieth-percentile TEQ values ranged from 326 fg/m³ at the Jonquière site to 16 fg/m³ at Kejimkujik. Octa-PCDD is the most abundant isomer and was detected in all samples, followed by hepta-PCDD and hepta and octa-PCDF. Maximum concentrations of 73 pg/m³ of total PCDD, 37 pg/m³ of total PCDF and 1.95 pg/m³ TEQ were recorded during the program. The isomer 2,3,7,8-T_4CDD was detected in 28% of the samples with a median concentration of 3 fg/m³ and a maximum of 61 fg/m³. Although the octa and hepta congeners are most abundant they are also the least toxic and make only a small contribution to TEQ. Four isomers, 2,3,4,7,8-P_5CDF, 2,3,7,8-T_4CDF, 1,2,3,7,8-P_5CDD and 1,2,3,4,7,8-H_6CDF, account for 65% of computed TEQ.

Polycyclic aromatic hydrocarbons, polychlorinated dibenzo-*p*-dioxins and dibenzofurans are ubiquitous in air samples collected in rural and urban locations in Canada. Mean total PAH concentrations vary by almost three orders of magnitude between remote rural sites and source impacted urban locations while mean PCDD/PCDF concentrations (expressed as 2,3,7,8-T_4CDD toxic equivalents vary by a factor of 20. While there has been some apparent reductions in air concentrations over the past ten years, it is clear that there are still numerous sources of these toxic substances in Canada. These sources create both immediate and long range impacts. Additional efforts are required in characterizing and quantify emission releases of PAH and PCDD/PCDF and in determining the impact of specific sources on measurement sites. Because of the many known harmful effects of these classes of substance, it would be prudent to accelerate efforts to reduce environmental exposures.

Sommaire

La Division de l'analyse et de la qualité de l'air (Protection de l'environnement, Environnement Canada) fait partie du Réseau national de surveillance de la pollution atmosphérique (RNSPA) et, à ce titre, s'occupe de mesurer les hydrocarbures aromatiques polycycliques (HAP), les polychlorodibenzo-*p*-dioxines (PCDD) et les polychlorodibenzofuranes (PCDF) dans l'air ambiant. Avec la collaboration des services environnementaux provinciaux et municipaux et des bureaux régionaux d'Environnement Canada, nous avons fait des échantillonnages dans 39 stations de surveillance situées en zone urbaine et en zone rurale dans les diverses régions du Canada. Le rapport présenté ici résume les résultats concernant la période qui va de 1987 à 1997 (la plupart des données ont été recueillies entre 1995 et 1997).

Depuis une trentaine d'années, le groupe des HAP a suscité passablement d'intérêt, car certains de ces composés sont cancérogènes pour l'humain. Comme les HAP résultent de la combustion incomplète des combustibles fossiles, ils sont présents partout dans l'atmosphère. Dans l'inventaire des émissions de HAP relevées au Canada en 1990, les alumineries, le chauffage au bois des habitations, les feux à ciel ouvert et les véhicules à moteur diesel sont les principales sources anthropiques de HAP. Les HAP émis au cours des incendies forestiers représentent 46 % des émissions totales inventoriées, mais leur contribution à la concentration moyenne de HAP dans l'air ambiant est généralement modeste. Certains HAP figurent sur la liste des substances d'intérêt prioritaire de la *Loi canadienne sur la protection de l'environnement* (LCPE); 5 composés de ce groupe (benzo(a)pyrène, benzo(b)fluoranthène, benzo(j)fluoranthène, benzo(k)fluoranthène et indéno(1,2,3-cd)pyrène) sont dits « toxiques » au sens défini à l'article 11c (substances qui constituent un danger pour la vie ou la santé humaine). Par ailleurs, neuf HAP (acénaphtène, fluorène, phénanthrène, anthracène, fluoranthène, pyrène, benz(a)anthracène, benzo(a)pyrène et naphtalène) ont été désignés toxiques au sens défini à l'article 11a (substances qui ont un effet nocif sur l'environnement).

Dans de nombreuses études, on signale que les PCDD et les PCDF, en raison de leur toxicité pour les animaux, de leur persistance et de leur bioaccumulation, présentent un danger important pour la santé humaine et pour l'environnement. Sur 210 PCDD et PCDF, ce sont les dérivés de substitution en 2,3,7,8 qu'il y a surtout lieu de surveiller en raison de leurs effets sur la santé et sur l'environnement. Parmi les composés formant ce sous-groupe, l'isomère 2,3,7,8-TCDD s'est révélé le plus toxique pour les mammifères. Les PCDD et les PCDF ne sont ni produits ni utilisés intentionnellement : ce sont des contaminants ou des sous-produits de la fabrication et de la combustion des substances organochlorées. Dans l'inventaire des émissions de dioxine, furane et hexachlorobenzène que le Comité consultatif fédéral-provincial de la *Loi canadienne sur la protection de l'environnement* a récemment produit, l'incinération était à l'origine de 60 % des émissions de PCDD et de PCDF en 1990.

Les données dont nous disposons concernent quelque 2 200 échantillons de HAP obtenus par des prélèvements de 24 heures effectués dans 35 stations d'échantillonnage. On constate que les concentrations moyennes de HAP varient de plus de trois unités de grandeur entre les stations éloignées ou de zone rurale du parc Jasper et celle de la zone d'influence industrielle de Jonquière (la plage des moyennes va de 0,9 à 801 ng/m^3 et les valeurs du 90^e percentile vont de 4,8 à 2 650 ng/m^3). Pour ce qui est des stations situées en zone urbaine (pour lesquelles on

compte plus de 10 jours d'échantillonnage), les concentrations moyennes de HAP totaux varient de 10 à 65 ng/m^3, et les valeurs du 90^e percentile vont de 14 à 115 ng/m^3. En général, c'est dans les zones les plus populeuses qu'on trouve les moyennes les plus élevées avec les concentrations de HAP les plus fortes dans le 90^e percentile. Les maximums, tant pour les concentrations moyennes que pour les valeurs du 90^e percentile, ont été mesurés dans les stations situées à proximité de sources d'émissions industrielles (ou de fumée de combustion de bois, dans le cas de la station de Whitehorse). Avec une fréquence de détection allant de 94 % à 99,9 %, le phénanthrène, le fluoranthène, le pyrène, le benzo(b)fluoranthène, le benzo(k)fluoranthène et le benzo(j)fluoranthène sont les composés les plus abondants. Le 3-Mé-cholanthrène et le 7-Mé-benz(a)anthracène ont eu la fréquence de détection la plus faible. Globalement, les composés à l'état gazeux représentent l'essentiel de la masse de HAP, les formes à l'état de particules étant beaucoup moins abondantes.

Pour les stations sur lesquelles les données remontaient le plus loin (Jonquière, Montréal, Toronto, Hamilton et Windsor) nous avons déterminé les variations annuelles de l'ensemble des HAP toxiques (dangereux pour la santé) au sens de la *Loi canadienne sur la protection de l'environnement*. À Jonquière, les concentrations moyennes ont baissé dans une mesure considérable durant la période d'étude, les valeurs des 75^e et 90^e percentiles diminuant dans une proportion moindre. À Hamilton, on a constaté une variation substantielle d'une année à l'autre, mais la concentration moyenne de 1996 est la même que celle de 1989. À Montréal, la tendance semble à la hausse, tandis qu'à Toronto, les concentrations moyennes ont sensiblement baissé de 1994 à 1996.

Pour la recherche des PCDD et des PCDF, plus de 500 échantillons ont été obtenus par des prélèvements de 24 heures dans 34 stations de surveillance, dont 344 de 1994 à 1997. Dans bien des cas, toutefois, les données concernant une station ne portent que sur 2 ou 3 jours. Les seules stations pour lesquelles les données concernent une longue période sont celles de Windsor-University Av. (1989-1995), de Windsor-College (1990-1997) et de l'île Walpole (1989-1995). Globalement, les concentrations moyennes d'équivalent toxique (TEQ) (avec substitution 0,5-DL) varient de 105 fg/m^3 (station de Toronto) à 10 fg/m^3 (station de St. Andrews, au Nouveau-Brunswick). Dans le cas des stations où l'on a fait plus de 10 jours d'échantillonnage, les valeurs de TEQ dans le 90^e percentile vont de 326 fg/m^3 (station de Jonquière) à 16 fg/m^3 (station de Kejimkujik). L'octa-PCDD, mis en évidence dans tous les échantillons, est l'isomère le plus abondant; il est suivi de l'hepta-PCDD, de l'hepta-PCDF et de l'octa-PCDF. Les concentrations maximales mesurées au cours du programme sont les suivantes : PCDD total, 73 pg/m^3; PCDF total, 37 pg/m^3; TEQ, 1,95 pg/m^3. L'isomère 2,3,7,8-T_4CDD a été détecté dans 28 % des échantillons; sa concentration moyenne est de 3 fg/m^3 et sa concentration maximale, de 61 fg/m^3. Les composés octa et hepta, très abondants, sont les moins toxiques, si bien qu'ils ne contribuent que dans une faible mesure à l'équivalent toxique. Quatre isomères, soit le 2,3,4,7,8-P_5CDF, le 2,3,7,8-T_4CDF, le 1,2,3,7,8-P_5CDD et le 1,2,3,4,7,8-H_8CDF, sont à l'origine de 65 % de l'équivalent toxique.

On a trouvé des hydrocarbures aromatiques polycycliques, des polychlorodibenzo-*p*-dioxines et des polychlorodibenzofuranes partout dans les stations rurales et urbaines. Les concentrations moyennes de HAP totaux varient de presque trois ordres de grandeur entre les stations éloignées de zone rurale et celles des régions urbaines situées dans la zone d'influence de sources

d'émissions; quant aux concentrations moyennes de PCDD et de PCDF (exprimées en équivalents toxiques de 2,3,7,8-T_4CDD), elles varient d'un facteur de 20. Les concentrations de ces substances toxiques semblent avoir baissé ces dix dernières années, mais il ne fait aucun doute que les sources restent nombreuses au Canada. Par ailleurs, ces émissions exercent leurs effets autant dans les environs immédiats qu'à grande distance. Il faudra encore du travail pour caractériser et quantifier les émissions de HAP, de PCDD et de PCDF et pour mesurer leur impact de certaines des sources dans les lieux surveillés. Vu les nombreux effets nocifs de ces substances, la prudence conseille d'accélérer la mise en oeuvre des mesures visant à réduire les risques d'exposition environnementale.

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Most field sampling was carried out by staff of provincial and municipal environment agencies and by Environment Canada regional offices. The expanded 1994 to 1997 field sampling effort was coordinated by Steve Beauchamp, Rob Tordon and Clark Wiseman (Atlantic), Anita Wong (Ontario), Renata Bailey (Prairie and Northern) and Wayne Belzer (Pacific and Yukon). The Pt. Petre site is part of the Integrated Atmospheric Deposition Network (IADN) and the Kejimkujik site is part of the Canadian Air and Precipitation Monitoring Network (CAPMoN).

The sampling units used in the field were designed by Jim Mar of Analysis and Air Quality Division (AAQD), ETC, Ottawa and were constructed and deployed by Luc White and Ross Hodgson. Shipment of samples to the field, field data logging and transfer of samples for analysis was coordinated by Adrian Steenkamer, Claude Tremblay and Katherine Bridger of AAQD. Mylaine Tardif of AAQD provided the analytical method descriptions and supporting tables.

All PAH and PCDD/PCDF analyses were carried out by staff of AAQD as noted below:

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Introduction

As a component of the National Air Pollution Surveillance (NAPS) network, the Analysis and Air Quality Division (AAQD), Environmental Protection, Environment Canada operates an ambient air measurement program for polycyclic aromatic hydrocarbons, polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). With the co-operation of provincial and municipal environment agencies and Environment Canada regional offices, samples have been collected at thirty-nine urban and rural monitoring sites across Canada. This reports provides summary statistics for measured species for the period 1987 to 1997 (most data collected between 1995 and 1997). The importance of PAH and PCDD/PCDF in terms of the current Environment Canada toxics management program is also discussed. Sites are compared based on location (rural, suburban and urban) and in terms of source influences. An examination of trends in measurements for sites with the longest data record is also provided.

Sampling Sites and Schedules

A list of PAH and PCDD/PCDF sampling sites is provided in *Table 1*. The start and end date of sampling and the number of samples collected by parameter are shown (for all available data summarized in this report). The location of the site (rural, urban or suburban) and an indication of a potential point source influence are also provided in the Table. In some cases point sources are inferred based on monitoring results. Most of the thirty-nine sites are located in urban areas but eleven sites were in rural locations. Maps of monitoring site locations are provided in *Figures 1 and 2*.

Prior to December 1994, sampling was carried out at only the Windsor, Walpole Island, Montreal, Hamilton, Toronto and Jonquière sites with the majority of PCDD/PCDF samples collected at the Windsor area sites as part of the Detroit incinerator-monitoring program[1,2,3,4]. Samples are normally collected over 24 h sampling periods (midnight to midnight) although some 48-h sampling was carried out at the Windsor area sites during 1990 and 1991 and at the Powell River site. PAH samples were usually collected once every 12 days and PCDD/PCDF samples once every twenty-four days. At sites with a point source located nearby, samples were sometimes collected only on days with wind direction from the source (some samples at Ft. McMurray, Ft. Saskatchewan, Powell River and Winnipeg – Weston were collected this way). The sampling in Whitehorse – Riverdale was carried out on days with a noticeable wood smoke impact on air quality. Samples from Jasper-Hinton were collected either over 24 hours from 8:00 AM to 8:00 AM or over 7 days using daily 8-h sampling periods (8:00 AM to 4:00 PM).

Figure 1: PAH and PCDD/PCDF Monitoring Site Locations (Eastern Canada)

Figure 2: PAH and PCDD/PCDF Monitoring Site Locations (Western Canada)

Table I: Monitoring Site Locations

NAPS	Type[1]	Ind.[2]	Province	City	Address	Latitude	Longitude	Start Date	End Date	No. of Samples	
										PAH	PCDD/PCDF
20101	U		Prince Edward Island	Charlottetown	56 Fitzroy	46.24	63.13	21-May-95	18-Sep-95	6	3
30118	U		Nova Scotia	Halifax	1657 Barrington Street	44.65	63.57	02-Jun-95	18-Sep-95	6	2
30501	Ru		Nova Scotia	Kejimkujik	National Park	44.44	65.21	16-Dec-94	17-Jun-97	66	19
40203	S	R	New Brunswick	Saint John	Forest Hills	45.31	66.01	09-Jan-95	16-Dec-95	5	2
40901	Ru		New Brunswick	St. Andrews		45.09	67.08	09-Jan-95	09-Jul-97	47	19
50902	U	AS	Québec	Jonquière	Powell	48.44	71.20	04-Apr-89	16-May-97	188	18
50104	U	R	Québec	Montréal	1125 Ontario Est	45.52	73.56	04-Apr-89	25-Oct-97	223	25
64601	Ru		Ontario	Pt. Petre		43.83	77.15	31-Aug-96	15-Jun-97	31	10
60418	U		Ontario	Toronto	Junction Triangle	43.67	79.45	09-Feb-89	10-May-97	204	27
60512	U	IS	Ontario	Hamilton	Elgin & Kelly	43.26	79.86	25-Nov-88	19-Sep-97	204	31
62601	Ru		Ontario	Simcoe	Experimental Farm	42.88	80.29	19-Aug-96	10-May-97	29	11
60204	U	IS	Ontario	Windsor	467 University Ave. West	42.32	83.04	26-Jul-87	15-Apr-95	288	87
60211	U	IS	Ontario	Windsor	College & South St.	42.29	83.08	04-Jul-90	02-Aug97	236	91
61901	Ru		Ontario	Walpole Island		42.41	83.54	22-Jan-88	22-Mar-95	237	67
70119	U		Manitoba	Winnipeg	65 Ellen Street	49.90	97.15	03-Apr-95	13-Oct-97	68	26
70121	S		Manitoba	Winnipeg	301 Weston St.	49.80	97.10	21-Jan-95	07-Mar-95	5	3
80110	U		Saskatchewan	Regina	2505 11th. Avenue	50.45	104.62	21-Apr-95	25-Aug-95	8	4
80501	U	R	Saskatchewan	Estevan	1 St. & 14th Ave.	49.14	103.00	16-Dec-94	09-Apr-96	14	3
80401	U		Saskatchewan	Prince Albert	1257-1st Ave. E.	53.20	105.75	14-Feb-95	16-Apr-95	6	5
80601	U	R	Saskatchewan	Lloydminster	44th St. & 48th Ave.	53.28	110.00	05-Mar-96	02-Apr-96	4	-
-	Ru		Saskatchewan	Gray		50.20	104.40	28-May-96	07-Oct-96	9	4
90121	S	R, Pe	Alberta	Edmonton	17 Street & 105 Avenue	53.55	113.37	16-Dec-94	01-Oct-97	75	21
90130	U		Alberta	Edmonton	10255 - 104th Street	53.54	113.50	09-Apr-95	27-May-95	4	2
90601	S	Pe	Alberta	Fort Saskatchewan	100 Avenue & 98th Street	53.71	113.22	16-Dec-94	02-Feb-95	5	5
90801	U	R	Alberta	Fort McMurray	Macdonald Dr.	56.73	111.39	09-Apr-95	27-May-95	5	2
-	Ru		Alberta	Jasper Park	Snaring Warden Sta.	53.08	118.04	9-Feb-95	28-Mar-95	8	-
-	Ru		Alberta	Jasper Park	Miette Hot Springs	53.08	117.46	2-Feb-95	17-Feb-95	2	-
-	Ru		Alberta	Jasper -Hinton	Jasper-Hinton	53.19	117.45	26-Feb-95	30-Mar-95	8	-
	Ru		Alberta	Jasper -Hinton	Hinton Airport	53.22	117.42	20-Feb-95	28-Feb-95	2	-
	S		Alberta	Hinton	Hinton	53.25	117.34	21-Mar-95	28-Mar-95	2	-
102201	S	LS	British Columbia	Trail	Butler Park	49.10	117.69	16-Dec-94	28-Mar-95	5	2
101101	S		British Columbia	Chilliwack	Works Yard	49.15	121.95	15-May-95	19-Aug-95	5	2
100110	S		British Columbia	Vancouver	Hastings & Kensington	49.28	122.97	03-May-96	15-Jun-97	29	12
100111	S	R	British Columbia	Vancouver	Moody & Esplanade	49.28	122.85	11-Dec-95	8-Jun-96	14	3
100118	U		British Columbia	Vancouver	2550 W 10th Ave.	49.26	123.16	11-Dec-95	16-Apr-97	17	1
101201	Ru		British Columbia	Vancouver	Pitt Meadows	49.21	122.71	16-Dec-94	19-Aug-95	9	4
100303	U		British Columbia	Victoria	1250 Quadra St.	48.43	123.36	08-Jun-95	19-Aug-95	4	1
102301	U	PP	British Columbia	Powell River	Cranberry R.	49.87	124.52	14-Jul-96	23-Mar-97	30	12
119002	S	WS	Yukon	Whitehorse	Riverdale	60.72	135.05	11-Jan-95	04-Mar-95	5	2

[1] U - Urban , S - Suburban, Ru – Rural[2] R- Refinery, AS - Aluminum Smelter, IS - Iron & Steel, Pe - Petrochemicals, LS - Lead Smelter, PP - Pulp & Paper, WS - Wood Smoke

Methodology

Sampling

A filter-sorbent sampling system is used to collect particulate plus vapor-phase PAH and PCDD/PCDF as illustrated in *Figure 3*. The sampler is based on a high-volume sampler but is modified by AAQD staff to include a dry-gas meter or a rotary vane meter to record total sample volume.[5] The sampler uses a 20 by 25 cm Pallflex Teflon-coated glass fibre filter and polyurethane foam (PUF) sorbent. The sorbent cartridge is 7.5-cm diameter with a bed depth of 15 cm (two 7.5-cm deep PUF plugs). Samples are normally collected over 24 h with a typical sample volume of 600-800 m^3.

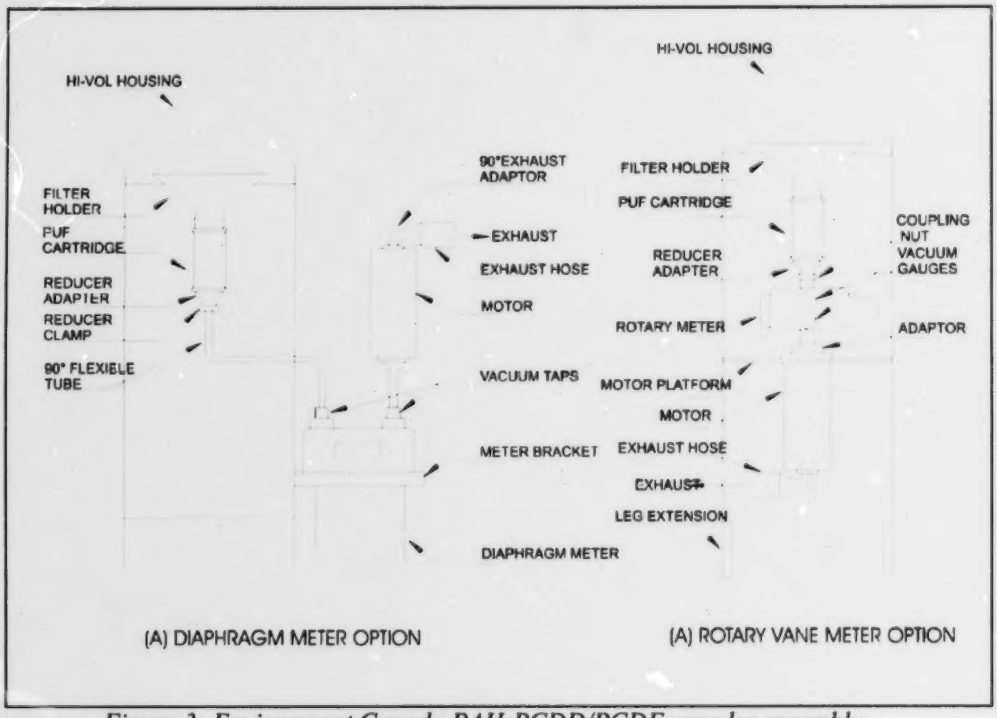


Figure 3: Environment Canada PAH-PCDD/PCDF sampler assembly.

Filters were used directly as received from the manufacturer. New PUF plugs were soxhlet extracted for 16 to 20 h using methanol followed by cyclohexane. The extracted plugs were then air-dried in a fume-hood and later inserted into the cartridge assembly before shipment to the field.

In the field, the filters and cartridges were mounted and the sampler was leak-checked before each sampling event. Typically the units were set to automatically collect a 24-h sample on the

prescribed sampling day. Filters and cartridges were normally installed one to six days before sampling and removed from one to six days after sampling. Field blanks were obtained at each site by mounting clean filters and PUF cartridges in the sampler and leaving them for a time period typical of that of an active sample.

Following sampling, filters and foams were sent by courier to the Ottawa lab where they were sealed and placed in a freezer until extraction. Sample data sheets were received with each sample and included total sample volume, gas meter vacuum, sample and station IDs, date and elapsed time.

PAH Analysis

The filter and PUFs are extracted together in order to measure the total (vapor plus particulate) PAH content of each sample. The sample filter is folded in four and placed at the bottom of a large clean soxhlet body followed by the PUFs. The surface of the top foam plug is spiked with 1000 ng each of 7 isotopically-labelled PAH compounds. The sample is extracted for 16-20 hours in cyclohexane (approx. 700 mL) at a rate of 3-5 cycles/hour. The raw extract is then filtered through Na_2SO_4 and concentrated to a volume of 1 to 2 mL by rotary evaporation.

A cleanup column is constructed using an open column filled with activated silica gel and plugged with clean glass wool. The column is then topped with ~ 2 g (2 cc) of Na_2SO_4 and pre-washed with 10 mL of hexane. When the hexane has drained to bed level the raw extract is quantitatively transferred onto the column. The flask is rinsed with hexane three times (1 to 2 mL rinses) and each rinse is quantitatively transferred to the column.

The column is eluted with 5 mL of hexane, followed by 5 mL of benzene and the eluate is archived (aliphatic hydrocarbon fraction). The PAH is then eluted with two 5 mL aliquots of benzene into a calibrated centrifuge tube. The PAH fraction (benzene fraction) is concentrated to less than 0.9 mL by UHP nitrogen blow-down at ambient temperature in a fume-hood. After addition of 100 uL of d_{10}-fluoranthene (10 ng/uL), the purified sample extract is then reconstituted to a known volume (typically 1.0 mL) using benzene prior to GC/MS analysis.

PAH are separated and analyzed by capillary column gas chromatography / low resolution mass spectrometry (LRMS). The mass spectrometer is operated using electron impact ionization in the selected ion-monitoring mode (SIM). A minimum of two characteristic ions is monitored per target analyte. Target compound identification is confirmed when the analyte's characteristic ions are present in the right ratio at the appropriate retention times.

The final purified extract is analyzed under the following operating conditions:

Instrument: HP 5890 GC interfaced directly to HP 5970, 5971 or 5972 MSD.
Injection: 1 µL, cool on-column.
Column: 30 m DB-5 fused silica, 0.25 mm ID and 0.25 um film thickness (or equivalent or better).

Oven Temp: 90°C for 1 min, to 200°C at 20 C°/min, to 210°C at 1 C°/min, then to 280°C at 5 C°/min and hold for 15 min. (Temperature program may require modification for other column types or to improve resolution)
Detection Mode: Electron Impact Ionization @ 35 or 70 eV operated in the Selected Ion Monitoring (SIM) mode; 5-step program with one to three ions per compound, 50 ms dwell per ion.
Calibration: Calibration is performed using a standard PAH mixture containing 27 compounds at a concentration of 1 ng/µL of each compound (*Table II*).

Quantitation. The internal standard quantitation method was used for all target compounds. MS relative response factors determined for the standard mixture components on the same day were used to quantitate sample levels of target analytes. Although 27 compounds are present in the calibration standard, depending on the performance of the analytical column, some are unresolved therefore 25 individual results are reported for each sample. Important unresolved species are benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(j)fluoranthene and chrysene and triphenylene.

The limit of detection will vary depending upon the sampling site, sampling conditions, interferences, contaminants present and instrument sensitivity. The method detection limit (MDL) was obtained by replicate analysis of certified reference material (urban dust 1649). Based on a 1,000 m^3 sample of air and a final volume of 1.0 mL, the MDL for PAH ranges from 14 to 25 pg/m^3 per analyte.

PCDD/PCDF Analysis

Dioxin/Furan. The filter and PUFs are extracted together in order to measure the total (vapor plus particulate) PCDD/PCDF content of each sample. The sample filter is folded in four and placed at the bottom of a large clean soxhlet body followed by the PUFs. The sample is spiked with 1- 2 ng of the nine 2,3,7,8-substituted $^{13}C_{12}$-labeled PCDD/PCDF congeners (see *Table III*). The sample is then extracted for 16-20 hours using toluene. The dioxin/furan sample extract is filtered through anhydrous sodium sulphate, concentrated to ~ 2 mL exchanged to hexane and re-concentrated to ~ 2 mL. The concentrated extract is cleaned by passage through a series of two columns consisting of an acid coated, base coated and silver nitrate coated silica to eliminate easily oxidized organics and sulphurous compounds and to a basic alumina column to isolate PCDD/PCDF from potential interference. Extracts are then concentrated just to dryness under a gentle stream of nitrogen. The sample is then re-dissolved in 20 µL of a recovery standard solution containing 50 pg/µL of $^{13}C_{12}$-1,2,3,4-T_4CDD and $^{13}C_{12}$-1,2,3,7,8,9-H_6CDD. Samples are analyzed by High Resolution GC/HRMS. The MS is operated in electron impact (EI) and selected ion monitoring (SIM) modes.[6]

Dioxin/Furan/PAH. In addition to spiking the sample with 1000 ng of PAH surrogates, the sample is spiked with 2 - 4 ng of the nine 2,3,7,8-substituted $^{13}C_{12}$-labeled PCDD/PCDF congeners (see Table III). The sample is extracted for 16-20 hours with cyclohexane/toluene (80/20). The raw extract is split into two fractions one for PAH cleanup/analysis and one for PCDD/PCDF cleanup/analysis.

Table II: Quantitation Standard and Monitored Ions for PAH Analysis

Compounds	Abbreviation	Quantitation Ion	Confirmation Ions	Relative Intensity
Acenaphthylene	AL	152	151, 150	100, 24, 13
Acenaphthene	AE	153	154, 152	100, 53, 21
Fluorene	FL	166	165, 163	100, 91, 18
2-Me-fluorene	MFL	165	180, 178	100, 27, 27
Phenanthrene	PHE	178	176, 179	100, 19, 16
Anthracene	AN	178	176, 179	100, 18, 16
Fluoranthene	FLT	202	200, 101	100, 21, 13
Pyrene	PY	202	200, 101	100, 21, 13
Benzo(a)fluorene	B(a)FL	216	215, 108	100, 77, 8
Benzo(b)fluorene	B(b)FL	216	215, 108	100, 93, 9
1-Me-pyrene	MPY	216	215, 108	100, 73, 7
Benzo(ghi)fluoranthene	B(ghi)F	226	224, 113	100, 24, 11
Benz(a)anthracene	B(a)A	228	226, 114	100, 27, 8
Chrysene/Triphenylene	C&T	228	226, 114	100, 29, 7
7-Me-Benz(a)anthracene	MB(a)A	242	241, 239	100, 12, 5
Benzo(b+k+j)fluoranthene	B(b+k+j)F	252	250, 126	100, 24, 9
Benzo(e)pyrene	B(e)P	252	250, 126	100, 30, 8
Benzo(a)pyrene	B(a)P	252	250, 126	100, 25, 10
Perylene	PER	252	250, 126	100, 29, 10
3-Me-cholanthrene	MCH	268	252, 126	100, 34, 10
Indeno(1,2,3-cd)pyrene	IP	276	274, 138	100,21,10
Dibenz(ah)anthracene	D(ah)A	278	276, 139	100, 39, 7
Benzo(b)chrysene	B(b)C	278	276, 139	100, 28, 6
Benzo(ghi)perylene	B(ghi)P	276	274, 138	100, 22, 11
Anthanthrene	ANT	276	274, 138	100, 20, 10
Isotopically-labelled surrogates				
Acenaphthene-d_{10}				
Anthracene-d_{10}	*AE	164	NA	
Pyrene-d_{10}	*AN	188	NA	
Benz(a)anthracene-d_{12}	*PY	212	NA	
Benzo(a)pyrene-d_{12}	*B(a)A	240	NA	
Dibenz(ah)anthracene-d_{14}	*B(a)P	264	NA	
Benzo(ghi)perylene-d_{12}	*B(ah)A	292	NA	
	*B(ghi)P	288	NA	
Internal Standard				
Fluoranthene-d_{10}	IS	212	NA	

Table III: Composition of PCDD/PCDF Surrogate Solution

Surrogate	Amount Spiked (ng)
$^{13}C_{12}$-2,3,7,8-TCDD	1
$^{13}C_{12}$-2,3,7,8-TCDF	1
$^{13}C_{12}$-1,2,3,7,8-P_5CDD	1
$^{13}C_{12}$-1,2,3,7,8-P_5CDF	1
$^{13}C_{12}$-1,2,3,6,7,8-H_6CDD	1
$^{13}C_{12}$-1,2,3,4,7,8-H_6CDF	1
$^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDD	1
$^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDF	1
$^{13}C_{12}$-OCDD	2

The final purified extract is analyzed under the following operating conditions:

Instrument: VG-70S/Autospec HRGC/HRMS operated in the electron impact (28 to 40 eV) and selected ion monitoring modes with a dwell time of 100 msec/ion tuned to a minimum of 5000 - 10000 resolving power.
Column: DB-5 (or equivalent), 60m x 0.25 mmID with 0.25 µm film.
Injection: 2 µL, on-column or split/splitless.
Oven Temp: Initial temperature of 100 °C for split/splitless and 70 °C for on-column hold for 1 min; then from 100 (or 70) to 200 °C at 40 C°min^{-1}; from 200 to 235 °C at 3 C°min^{-1}; hold at 235 °C for 10 min., 235 to 310 °C at 8 C°min^{-1}; and hold at 310 °C for 15 min (temperature program may require modification for other column types or to improve resolution).

An internal standard method is used to quantify PCDD/PCDF based on the use of average RRF over the calibration range represented by the standard solutions defined in *Table IV*. For native standards, the RRF is the ratio of analyte response factor to the response factor of the corresponding labeled surrogate[6,7]. Using these RRFs recovery-corrected concentrations for PCDD/PCDF in samples are calculated directly. The RRF of the surrogate response factor to the response factor of the corresponding recovery standard is used to calculate surrogate recoveries in samples. The ion masses used in the identification and measurement of target analytes are specified in *Table V*.

The method detection limit (MDL) was obtained by replicate analysis of certified reference material (urban dust 1649). Based on a 1000 m^3 sample of air and a final volume of 20 µL, the MDL for PCDD/PCDF ranges from 1to 4 fg/m^3 per analyte detected.

Table IV: Composition of PCDD/PCDF Calibration Solutions (CS)

PCDD/PCDF Standard	pg/µL (in toluene)			
	CS1[a]	CS2	CS3[b]	CS4
Native standards [c,d]				
2,3,7,8-T_4CDD	0.25	1	5	25
1,2,3,7,8-P_5CDD	0.25	1	5	25
1,2,3,4,7,8-H_6CDD	0.50	2	10	50
1,2,3,6,7,8-H_6CDD	0.50	2	10	50
1,2,3,7,8,9-H_6CDD	0.50	2	10	50
1,2,3,4,6,7,8-H_7CDD	0.50	2	10	50
O_8CDD	1	4	20	100
2,3,7,8-T_4CDF	0.50	2	10	50
1,2,3,7,8-P_5CDF	0.50	2	10	50
2,3,4,7,8-P_5CDF	0.50	2	10	50
1,2,3,4,7,8-H_6CDF	0.50	2	10	50
1,2,3,6,7,8-H_6CDF	0.50	2	10	50
2,3,4,6,7,8-H_6CDF	0.50	2	10	50
1,2,3,7,8,9-H_6CDF	0.50	2	10	50
1,2,3,4,6,7,8-H_7CDF	0.50	2	10	50
1,2,3,4,7,8,9-H_7CDF	0.50	2	10	50
O_8CDF	1	4	20	100
Surrogates				
$^{13}C_{12}$-2,3,7,8-T_4CDD	50	50	50	50
$^{13}C_{12}$-2,3,7,8-T_4CDF	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-P_5CDD	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-P_5CDF	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-H_6CDD	50	50	50	50
$^{13}C_{12}$-1,2,3,4,7,8-H_6CDF	50	50	50	50
$^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDD	50	50	50	50
$^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDF	50	50	50	50
$^{13}C_{12}$-O_8CDD	100	100	100	100
Recovery standards				
$^{13}C_{12}$-1,2,3,4-T_4CDD[e]	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-H_6CDD[f]	50	50	50	50

[a] also used to assess detection limits; [b] used daily to verify calibration and abundance ratios; [c] penta- and hepta-CDF, hexa-CDD/CDF isomers listed in order of elution on a DB-5 column; [d] a solution of native congeners at CS2 concentrations is used as a spiking solution for method performance tests; [e] retention time marker and recovery standard for tetra- and penta-CDD/CDF; [f] retention time marker and recovery standard for hexa- and hepta-CDD/CDF and OCDD.

Table V: Selected Ion Masses, Ion Type and Control Limits

Window Number	Compound	Quantification Ions (m/z) 1st	2nd	Ion Type	Control Limits for Isotope Ratio
1	T_4CDF	303.9016	305.8987	M/M+2	0.65 – 0.89
	$^{13}C_{12}$-T_4CDF	315.9419	317.9389	M/M+2	0.65 – 0.89
	T_4CDD	319.8965	321.8936	M/M+2	0.65 – 0.89
	$^{13}C_{12}$-T_4CDD	331.9368	333.9339	M/M+2	0.65 – 0.89
	H_6CDPE^*	375.8364	-	M+2	-
	PFK	316.9824	-	Lock	-
2	P_5CDF	339.8597	341.8567	M+2/M+4	1.32 – 1.78
	$^{13}C_{12}$-P_5CDF	351.9000	353.8970	M+2/M+4	1.32 – 1.78
	P_5CDD	355.8546	357.8516	M+2/M+4	1.32 – 1.78
	$^{13}C_{12}$-P_5CDD	367.8949	369.8919	M+2/M+4	1.32 – 1.78
	H_7CDPE^*	409.7974	-	M+2	-
	PFK	366.9792	-	Lock	-
3	H_6CDF	373.8208	375.8178	M+2/M+4	1.05 – 1.43
	$^{13}C_{12}$-H_6CDF	383.8639	385.8610	M/M+4	0.43 – 0.59
	H_6CDD	389.8157	391.8127	M+2/M+4	1.05 – 1.43
	$^{13}C_{12}$-H_6CDD	401.8559	403.8529	M+2/M+4	1.05 – 1.43
	O_8CDPE^*	445.7555	-	M+4	-
	PFK	380.9760	-	Lock	-
4	H_7CDF	407.7818	409.7789	M+2/M+4	0.88 – 1.20
	$^{13}C_{12}$-H_7CDF	419.8220	421.8191	M+2/M+4	0.88 – 1.20
	H_7CDD	423.7766	425.7737	M+2/M+4	0.88 – 1.20
	$^{13}C_{12}$-H_7CDD	435.8169	437.8140	M+2/M+4	0.88 – 1.20
	N_9CDPE^*	479.7165	-	M+4	-
	PFK	430.9728	-	Lock	-
5	O_8CDF	441.7428	443.7398	M+2/M+4	0.76 – 1.02
	O_8CDD	457.7378	459.7348	M+2/M+4	0.76 – 1.02
	$^{13}C_{12}$-O_8CDD	469.7780	471.7750	M+2/M+4	0.76 – 1.02
	$D_{10}CDPE^*$	513.6775	-	M+4	-
	PFK	454.9728	-	Lock	-

* response of the chlorinated diphenyl ether must be absent for PCDF determination as it has a similar isotope ratio

Quality Assurance

PAH. Previous studies[5,8] have documented that the collection efficiency of the sampling system is excellent for sample volumes under 2,000 m^3. The exception are the lightest PAH measured, acenapthene, acenapthylene and fluorene, which can have breakthrough volumes of less than 2,000 m^3 at temperatures greater than 10 °C. These compounds also exhibit the most variable recovery efficiencies. Final results are not recovery corrected based on internal surrogate recoveries but these recoveries are used as an indication of successful cleanup and extraction procedures (± 20%). Method blanks (including filter) are run with each sample batch. Field blanks show very low levels of PAH, with total PAH in field blanks generally less than 0.5 ng/m^3. Phenanthrene, fluoranthene and pyrene are the species that are most often found at levels above detection in method blanks and field blanks. Maximum blank concentrations are in the range of 0.01 to 0.05 ng/m^3.

Based on a multiple sampler inter-comparison study carried out in Edmonton, the overall precision (relative standard deviation) of the PAH measurements is estimated to be 10-20 % for concentrations above 0.1 ng/m^3. To ensure accuracy, replicate analyses of certified reference material (urban dust SRM-1649) are carried out for each sample batch. The sampling and analytical methods closely match those proposed by the International Standards Organization (ISO)[9].

PCDD/PCDF. Collection efficiencies of the sampler for tetra through octa-PCDD and PCDF are expected to be near 100%. All reported PCDD/PCDF results are corrected based on the recovery of the labeled surrogates. Method blanks are performed in the same fashion as for PAH. No detectable levels of any PCDD or PCDF isomers were found in method blanks (detection levels of 1 to 4 fg/m^3). Only octa-PCDD was routinely detected in field blanks with measured levels generally less than 60 fg/m^3 at urban sites and less than 20 fg/m^3 at rural sites.

Based on a multiple sampler inter-comparison study carried out in Edmonton, the overall precision of the PCDD/PCDF measurements is estimated to be 10-20 % for concentrations above 5 fg/m^3.

Results and Discussion

Background

PAH. The category of compound known as PAH has received a good deal of attention over the last thirty years because some species of PAH are known human carcinogens. Because PAH result from the incomplete combustion of fossil fuels they are ubiquitous in the atmosphere. Based on an inventory of Canadian emissions of PAH[10] for 1990 (see *Table VI*) the primary anthropogenic sources of PAH are aluminum smelting, residential wood combustion, open air burning and diesel motor vehicles. Forest fires account for 46% of total emissions in the inventory, but their impact on average measured ambient PAH concentration is generally small.

Table VI: Sources of PAH Emissions in Canada (1990).

Source	Emissions (t/y)	% of Total
Forest fires	2,008	45.8
Aluminum plants	925	21.1
Residential heating with wood	474	10.8
Open air burning – brushwood	357	8.1
Incineration – teepee burners	249	5.7
Road transportation - diesel	155	3.5
Hydrocarbon spills	76	1.7
Road transportation – gasoline	45	1.0
Industrial emissions (Coke ovens, iron & steel, asphalt plants and refineries)	35	0.8
Fuel combustion for heating (residential, commercial and institutional)	32	0.7
Industrial fuel combustion	27	0.6
Incineration	2	0.1
Other	1	0.1
TOTAL	4,386	100

The PAH measured in this program span a wide range of molecular weights and their physical properties vary accordingly. For air-sampling programs, vapor pressure is a particularly important property as compounds with low vapor pressure are usually associated with particulate matter and compounds with higher vapor pressures are found as vapors. *Table VII* provides example vapor pressures for the PAH and an indication of the phase in which they are normally found in ambient air. The sampling protocol followed in this program is not capable of accurately measuring phase distributions and only combined sample (particulate plus vapor) results are reported. A detailed discussion of vapor/particulate PAH distribution is found in Reference 5.

Also shown in *Table VII* is an indication of the importance of the PAH species in relation to health and environmental effects. PAH appeared on the Canadian Environmental Protection Act (CEPA)

priority substances list (PSL)[11,12,13] and five species (benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene and indeno([1,2,3-cd)pyrene) were designated 'toxic' as defined in Section 11c (constituting a danger to human life or health) of the Act. Nine PAH (acenapthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene and naphthalene) were found to be toxic under Section 11a (having a harmful effect on the environment). Sixteen PAH have been targeted by the U.S. Environmental Protection Agency (EPA) as priority pollutants and benzo(a)pyrene has been identified by the International Joint Commission (IJC) as a Tier I pollutant targeted for virtual elimination. The IJC identified anthracene and 17 PAH's as a group (including but not limited to benz(a)anthracene, benzo(b)fluoranthene, benzo(g,h,i)perylene, perylene and phenanthrene) as Tier II substances which have the potential for causing adverse impacts on the Great Lakes environment. PAHs are also to be included under the United Nations (UN) Environmental Commission for Europe (ECE) protocol on persistent organics pollutants (POPs)[14]. A suggested list of representative species for monitoring and reporting is shown in Table IV.

Table VII: Expected Phase of PAH and Potential Importance In Reference to Health and Environmental Effects

Compound	Phase	PSL Toxic	IJC	EPA	UN-ECE
Measured in Current Program					
Acenaphthylene	V			X	
Acenaphthene	V	Yes (11a)		X	
Fluorene	V	Yes (11a)		X	
2-Me-Fluorene	V				
Phenanthrene	V/P	Yes (11a)	Tier II	X	X
Anthracene	V/P	Yes (11a)	Tier II	X	X
Fluoranthene	V/P	Yes (11a)		X	X
Pyrene	V/P	Yes (11a)		X	X
Benzo(a)fluorene	V/P				
Benzo(b)fluorene	V/P				
1-Me-Pyrene	V/P				
Benzo(g,h,i)fluoranthene	V/P				
Benz(a)anthracene	V/P	Yes (11a)	Tier II	X	X
Chrysene&Triphenylene	V/P				X
7-Me-Benz(a)anthracene	P			X	
Benzo(b)&(k)&(j)fluoranthene	P	Yes (11c)	Tier II	X	X
Benzo(e)pyrene	P				X
Benzo(a)pyrene	P	Yes (11a&c)	Tier I	X	X
Perylene	P		Tier II		X
3-Me-Cholanthrene	P				
Indeno(1,2,3-cd)pyrene	P	Yes (11c)		X	X
Dibenz(a,c)&(a,h)anthracene	P			X	X
Benzo(b)chrysene	P				
Benzo(g,h,i)perylene	P		Tier II	X	X
Anthanthrene	P				
Other					
Naphthalene[1]	V	Yes (11a)		X	X
Dibenzo(a,i)pyrene	P				X
Retene	P				X

[1] measured in NAPS VOC program.

PCDD/PCDF. Numerous assessments of PCDD/PCDF have recognized that because of their toxicity to animals, their persistence and their ability to bio-accumulate, they represent a significant danger to human health and to the environment[15]. Of the 210 possible PCDD/PCDF congeners, it is the 2,3,7,8 substituted PCDDs and PCDFs that are of most concern from a health and environmental effects perspective. Of these, the 2,3,7,8-TCDD isomer has been shown to be the most toxic to mammals. Toxic equivalency factors (TEFs) which relate the toxicity of the other 2,3,7,8 substituted PCDD/PCDF isomers to 2,3,7,8-TCDD have been adopted by the Federal-Provincial Multi-media Guidelines Advisory Committee and Environment Canada. These factors are shown in *Table VIII.* PCDD/PCDF meet all the criteria for management under Track I of the Toxic Substances Management Policy (TSMP) and are targeted for virtual elimination from the Canadian environment[16]. They have also been designated as Tier I substances by the IJC and are included in the UN ECE draft POPs protocol.

Table VIII: Toxic Equivalency Factors for 2,3,7,8 Substituted PCDD/PCDF

Isomer	Toxic Equivalency Factor (TEF) Relative to 2,3,7,8-TCDD
2,3,7,8-T_4CDD	1.0
1,2,3,7,8-P_5CDD	0.5
1,2,3,4,7,8-H_6CDD	0.1
1,2,3,6,7,8-H_6CDD	0.1
1,2,3,7,8,9-H_6CDD	0.1
1,2,3,4,6,7,8-H_7CDD	0.01
OCDD	0.001
2,3,7,8-T_4CDF	0.1
1,2,3,7,8-P_5CDF	0.05
2,3,4,7,8-P_5CDF	0.5
1,2,3,4,7,8-H_6CDF	0.1
1,2,3,6,7,8-H_6CDF	0.1
2,3,4,6,7,8-H_6CDF	0.1
1,2,3,7,8,9-H_6CDF	0.1
1,2,3,4,6,7,8-H_7CDF	0.01
1,2,3,4, 7,8,9-H_7CDF	0.01
OCDF	0.001

There is no intentional production or use of PCDD/PCDF. They are released into the environment as contaminants or by-products associated with the production or combustion of chlorinated organic substances. *Table IX* shows recent emission estimate results for the United States[17,18] and Canada[19] in terms of percentage contributions from various source types to total PCDD/PCDF releases.

These isomers of PCDD and PCDF also span a wide vapor pressure range. At 20°C, the tetra and penta-PCDD and PCDF are found in both the particulate and vapor phase in the atmosphere while the other congener classes are found predominantly in the particulate phase. Only combined vapor plus particulate results are reported.

Table IX: Estimated Percentage Contribution of Sources to Air Emissions of PCDD/PCDF (TEQ)

Source Class	Cohen et al Canada & U.S. Great Lakes Region 1993 (% of Total)	Thomas & Spiro U.S. 1989 (% of Total)	CEPA-FPAC Inventory Canada 1990 (% of Total)
Medical waste incinerators	53	11	3.6
Municipal waste incinerators	24	48	35
Hazardous waste incineration	6	3.2	<0.1
Apt. incinerators & open garbage burning	-	19	-
Tepee Burners for Municipal Waste		-	20
Secondary copper smelters	5	-	-
Wood combustion	3.2	4.3	4.8
Iron sintering plants	2.8	-	12
Coal combustion	2.6	<0.1	<0.1
Cement kilns	2.1	-	6.2
Heavy duty diesel vehicles	1.5	<0.1	2.3
Sewage sludge incinerators	0.3	1.1	<0.1
Secondary copper refiners	0.1	3.2	-
Gasoline motor vehicles	0.1	<0.1	-
Dioxin contaminated chemical application	-	2.1	-
Forest & agricultural burning	-	4.6	-
Electric arc furnaces	-	-	2.5
Pulp & paper boilers	-	-	2.8
Industrial fuel Combustion	-	-	4.6
Other	-	1	5.7

Ambient Air PAH Concentrations

Data from approximately 2,200 daily PAH samples collected at 35 sites are available (1987 to 1997), however sampling days per site range from 1 to over 250. *Figure 4* shows mean, 10^{th} and 90^{th} percentile total PAH (sum of all 28 species measured) concentrations by site category for samples collected between 1994 and 1997. Means vary by more than three orders of magnitude from the rural-remote Jasper Park sites to the industrial influenced Jonquière site (for sites with 20 or more samples the range of means is 1.7 to 810 ng/m³ and the range of 90^{th} percentile values is 3.4 to 2,650 ng/m³). For the urban sites (with more than 10 sampling days of data) mean total PAH concentrations ranged from 10 to 65 ng/m³ with 90^{th} percentile concentrations ranging from 14 to 115 ng/m³. In general, the larger population areas experienced the highest mean and 90^{th} percentile PAH concentrations. The sites with industrial emission sources (or wood smoke in the case of the Whitehorse site) nearby recorded the highest mean and 90^{th} percentile concentrations. The 10^{th} percentile concentrations at most of these sites were similar to urban mean values. For the rural sites in Ontario, mean concentrations increased from Pt. Petre to Simcoe to Walpole Island.

Table X provides overall summary statistics and frequency of detection for all species for all sites for the 1987 to 1997 sampling period. The most abundant species were phenanthrene, fluoranthene, pyrene and benzo(b)&(k)&(j)fluoranthene with frequencies of detection ranging from 94 to 99.9%. In contrast the species with the lowest frequency of detection were 3-Me-cholanthrene and 7-Me-Benz(a)anthracene. Median species fractions for urban, rural and industrial (excluding Jonquière and Whitehorse) influenced sites are shown in *Figure 5a* for the seventeen most abundant PAH. As shown in the figure, despite large differences in concentrations, species profiles were quite similar at the three categories of sites with phenanthrene accounting for 60% or more of total PAH mass. Overall, vapor phase species account for most of the PAH mass with particulate phase species found in much lower concentrations. In *Figure 5b* the industrial site profile is compared to that of Whitehorse and Jonquière. PAH concentrations at these two sites are dominated by one specific source, wood smoke in the case of Whitehorse and aluminum smelting in the case of Jonquière. At these two sites, phenanthrene accounts for 20 to 30% of total PAH and particulate phase species account for a much larger fraction of total PAH than at more 'typical' sites.

As noted previously, five PAH species were found to be CEPA-toxic based on danger to human health during the PSL assessment. Summary statistics by site for the these PAH (benzo(a)pyrene, benzo(b)&(k)&(j)fluoranthene and indeno(1,2,3-cd)pyrene) are shown in *Tables XI, XII and XIII.* The distribution of measured concentrations is similar to that for total PAH with maximum concentrations of the species varying by more than four orders of magnitude from the lowest to the highest concentration site. Using data for all sites benzo(a)pyrene was detected in 74% of samples with a median concentration of 0.06 ng/m^3 and a 90th percentile concentration of 0.9 ng/m^3. Benzo(b)&(k)&(j)fluoranthene was detected in 91% of samples with median and 90th percentile values of 0.34 and 4.2 ng/m^3 respectively. Indeno(1,2,3-cd)pyrene was detected in 88% of all samples with a median concentration of 0.13 ng/m^3 and a 90th percentile value of 1.2 ng/m^3. A measurement program was carried out at the Toronto, Junction Triangle site[8] in 1984 – 1986, the mean concentration of benzo(a)pyrene was 0.3 ng/m^3 vs. 0.2 ng/m^3 in 1994 – 1997. The mean benzo(b)&(k)&(j)fluoranthene concentration was 1.3 ng/m^3 vs. 0.8 ng/m^3 in 1994 – 1997. Germain (1997) reported results for other sites impacted by aluminum smelters (Shawinigan and Baie Comeau)[20]. A maximum benzo(a)pyrene concentrations of 75 ng/m^3 and a maximum benzo(b)&(k)&(j)fluoranthene concentration of 260 ng/m^3 were measured at the Baie Comeau site.

For sites with the longest data records (Jonquière, Montréal, Toronto, Hamilton and Windsor) yearly variations in the sum of the CEPA toxic (health) PAH are shown in *Figure 6.* For Jonquière, median concentrations decreased substantially through the period with smaller decreases in 75th and 90th percentile values. The Hamilton site shows substantial year to year variation but the median concentration for 1996 was the same as for 1989. The Montreal site appears to be experiencing an upward trend whereas median concentrations at the Toronto site show a significant decline between 1994 and 1996. Seasonal variations in concentrations for these sites are shown in *Figure 7.* The urban sites show a characteristic seasonal pattern in concentration with the lowest values experienced in the summer. This is due to increased destruction of these species in the summertime due to reactions with ozone and hydroxyl radicals and due to reduced combustion of wood and other fuels (such as for residential heating) in the summer. This can be contrasted with the seasonal variation of phenanthrene as shown in *Figure 8.* At the urban sites, phenanthrene peaks in the summer months presumably due to increases in evaporative emissions from petroleum products

such as asphalt and roofing tar. At the two industrial influenced sites, monthly concentrations are more dependent on variations in meteorological variables, especially wind direction and wind speed.

Day of week variations in the CEPA toxic (health) PAH are shown in *Figure 9*. The Montréal and Toronto sites show a strong day of the week pattern with significantly higher concentrations on Wednesday and Thursday than on Saturday and Sunday. The Jonquière site experiences the highest median concentrations on Monday while the other sites show only small day of week variations in median concentration.

Figure 10 provides an indication of spatial variability of PAH concentrations from urban to rural sites between Windsor and Montréal. The bars represent average concentrations per site using data from 24 sampling days in 1996 and 1997 when all sites were operational. Typically the urban site concentrations are a factor of 8 to 25 times higher than nearby rural sites. This reflects the much higher PAH emission densities in the urban areas.

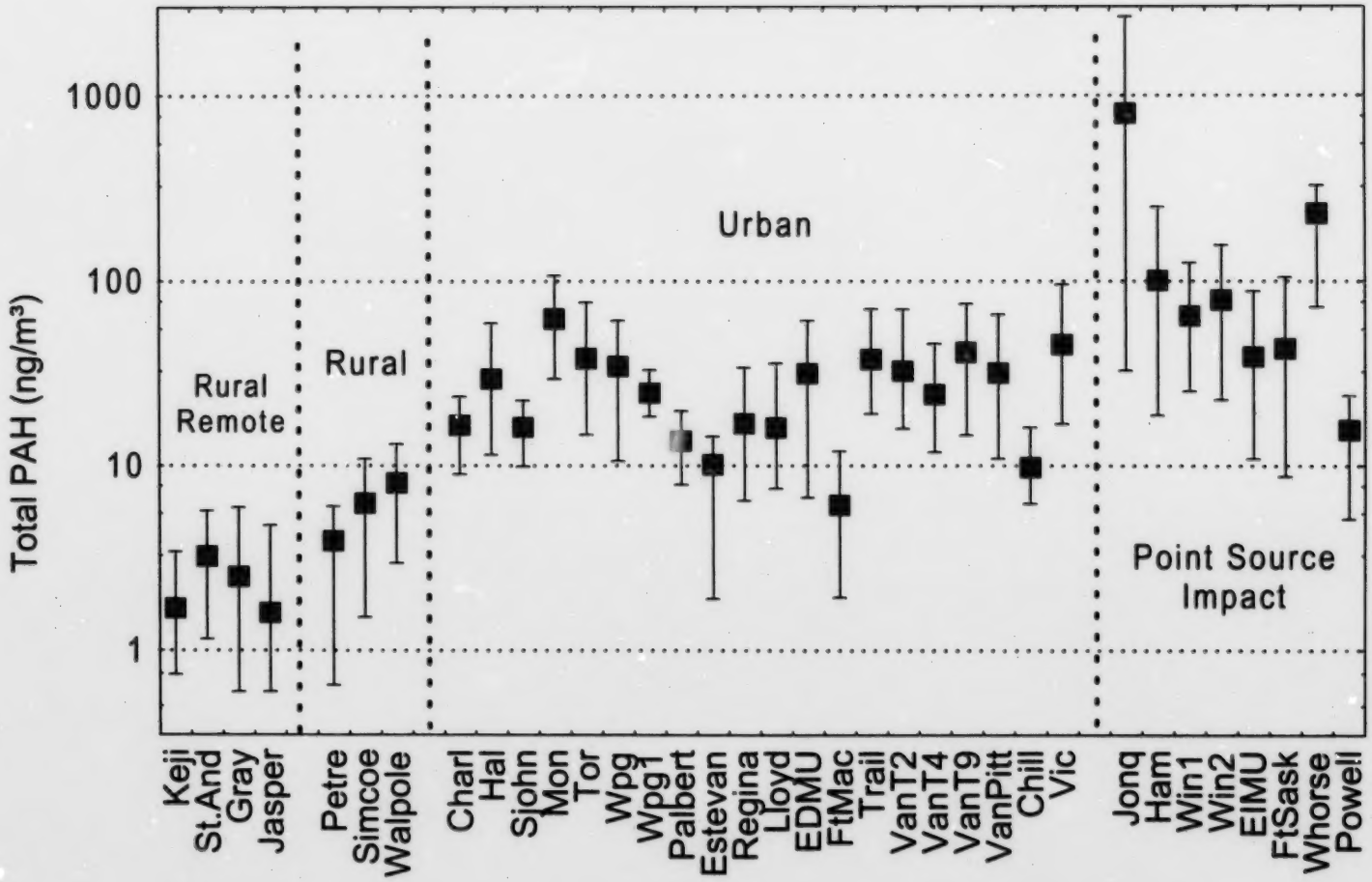


Figure 4: Mean, 10th and 90th Percentile Total PAH Concentrations (ng/m³) by Site (1994-1997)

Table X: Overall Summary Statistics (ng/m³) and Frequency of Detection for All PAH Species (All Data Collected Between 1987 and 1997).

COMPOUND	Number of Sampling Days	Frequency of Detection	Mean	Standard Deviation	Median	Maximum	Mean Detection Level
Acenaphthylene	2,195	93%	3.17	6.66	0.77	82.28	0.004
Acenaphthene	2,205	97%	5.59	29.93	1.10	854.84	0.004
Fluorene	2,205	98%	7.45	19.48	3.22	596.44	0.006
2-Me-Fluorene	2,205	89%	3.74	6.51	2.16	156.32	0.006
Phenanthrene	2,205	99.9%	40.17	133.73	13.39	2104.43	0.004
Anthracene	2,185	65%	3.39	15.89	0.37	425.54	0.004
Fluoranthene	2,205	99%	20.62	99.27	3.33	1805.02	0.006
Pyrene	2,205	99.5%	14.99	74.66	2.41	1235.24	0.007
Benzo(a)Fluorene	2,205	91%	2.63	13.71	0.28	244.16	0.006
Benzo(b)Fluorene	2,205	83%	0.92	4.38	0.11	92.65	0.005
1-Me-Pyrene	2,205	80%	0.60	2.93	0.10	53.42	0.004
Benzo(g,h,i)Fluoranthene	2,205	91%	0.98	4.53	0.25	144.91	0.005
Benz(a)Anthracene	2,205	82%	3.60	28.03	0.13	702.91	0.004
Chrysene&Triphenylene	2,205	96%	9.08	54.08	0.45	926.71	0.005
7-Me-Benz(a)Anthracene	2,200	2%	0.06	0.96	0.01	39.85	0.005
Benzo(b)&(k)&(j)fluoranthene	2,186	94%	12.02	70.02	0.56	1083.65	0.006
Benzo(e)Pyrene	2,205	92%	4.66	28.41	0.24	490.44	0.006
Benzo(a)Pyrene	2,179	81%	1.89	11.12	0.13	221.88	0.005
Perylene	2,204	50%	0.32	2.22	0.02	45.88	0.005
3-Me-Cholanthrene	2,200	1%	0.01	0.20	0.01	9.25	0.004
Indeno(1,2,3-cd)Pyrene	2,205	90%	1.97	10.40	0.21	194.22	0.005
Dibenz(a,c)&(a,h)Anthracene	2,205	41%	0.42	2.71	0.01	61.66	0.003
Benzo(b)Chrysene	2,205	29%	0.16	1.15	0.01	33.53	0.004
Benzo(g,h,i)Perylene	2,205	91%	1.99	9.64	0.29	148.54	0.005
Anthanthrene	2,204	36%	0.07	0.32	0.01	9.25	0.004
Total PAH	2,203	100.0%	139.91	579.09	35.25	9860.38	-

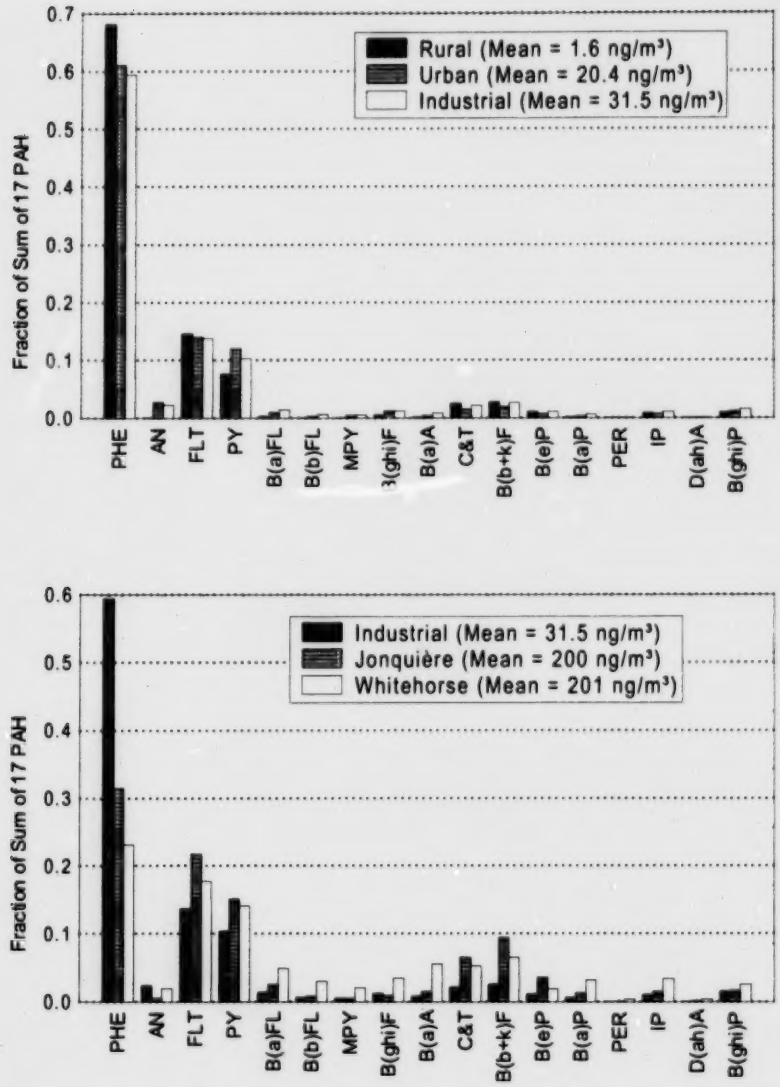


Figure 5: Typical Species Profiles at Rural, Urban, Industrially Influenced, Whitehorse and Jonquière Sites (17 most abundant PAH)

Table XI: Summary Statistics for Benzo(a)Pyrene (ng/m³) for All Monitoring Sites (1994 – 1997)

City	Address	No. of Samples	% Detect	Mean DL	10th Perc.	90th Perc.	Max.	Mean	Standard Deviation	Median
Charlottetown	56 Fitzroy St.	6	83%	0.02	0.01	0.04	0.04	0.02	0.01	0.03
Halifax	1657 Barrington St.	6	100%	-	0.02	0.10	0.10	0.04	0.03	0.04
Kejimkujik	National Park	66	17%	0.02	0.00	0.02	0.21	0.01	0.03	0.01
St. Andrews		47	30%	0.01	0.00	0.05	0.24	0.02	0.04	0.01
Saint John	Forest Hills	5	100%	-	0.08	0.24	0.24	0.15	0.07	0.15
Jonquière	Powell/Hoopes	83	87%	0.02	0.01	38.26	144.02	12.16	24.92	1.88
Montreal	1125 Ontario	95	92%	0.02	0.02	0.93	12.96	0.57	1.43	0.23
Pt. Petre		31	48%	0.01	0.00	0.07	0.37	0.04	0.08	0.01
Toronto	Junction Triangle	87	89%	0.01	0.01	0.47	1.05	0.19	0.20	0.14
Hamilton	Elgin/Kelly	92	100%	-	0.09	3.36	16.01	1.27	2.23	0.40
Simcoe	Experimental Farm	29	76%	0.02	0.01	0.11	0.14	0.04	0.04	0.03
Windsor	University Ave.	36	97%	0.01	0.10	0.87	2.11	0.36	0.39	0.25
Windsor	College/Prince	91	92%	0.02	0.04	0.51	2.06	0.26	0.31	0.18
Walpole		16	81%	0.02	0.01	0.11	0.28	0.05	0.07	0.04
Winnipeg	65 Ellen St.	68	76%	0.02	0.01	0.22	10.52	0.23	1.27	0.05
Winnipeg	301 Weston St.	5	100%	-	0.03	0.35	0.35	0.12	0.13	0.09
Prince Albert		6	50%	0.02	0.01	0.06	0.06	0.03	0.02	0.02
Estevan		14	57%	0.02	0.01	0.06	0.12	0.03	0.03	0.01
Regina	Longman Cresc.	8	75%	0.03	0.01	0.03	0.03	0.02	0.00	0.02
Lloydminster	5021-49 St.	4	25%	0.02	0.01	0.34	0.34	0.09	0.17	0.01
Gray		9	0%	0.02	0.01	0.01	0.01	0.01	0.00	0.01
Edmonton	17th St/105th Ave.	75	72%	0.02	0.01	0.39	1.90	0.14	0.29	0.05
Edmonton	10255-104th St.	4	75%	0.02	0.01	0.06	0.06	0.03	0.02	0.03
Fort Saskatchewan	9209A-96 Ave.	5	80%	0.01	0.00	0.91	0.91	0.38	0.48	0.07
Fort McMurray		5	60%	0.03	0.01	0.05	0.05	0.03	0.02	0.02
Jasper Park	Snaring Warden Sta.	8	25%	0.01	0.00	0.19	0.19	0.03	0.07	0.00
Trail	Butler Park	5	100%	-	0.09	0.56	0.56	0.23	0.20	0.11
Whitehorse	Riverdale	5	100%	-	2.27	8.23	8.23	6.00	2.48	6.48
Vancouver	2550 W 10th Ave.	17	82%	0.01	0.01	0.27	0.37	0.09	0.10	0.04
Vancouver	Kensington Park	28	36%	0.01	0.00	0.08	0.09	0.02	0.03	0.01
Vancouver	Rocky Point Park	14	79%	0.03	0.01	0.22	0.83	0.12	0.21	0.04
Vancouver	Pitt Meadows	9	78%	0.02	0.01	0.47	0.47	0.09	0.15	0.03
Chilliwack	Airport	5	20%	0.03	0.01	0.02	0.02	0.02	0.01	0.01
Powell River	Henderson School	30	60%	0.01	0.00	0.35	0.37	0.07	0.12	0.01
Victoria	1250 Quadra St.	4	100%	-	0.02	1.24	1.24	0.35	0.60	0.09
All Sites		1,119	74%	0.02	0.01	0.90	144.02	1.17	7.50	0.06

Table XII: Summary Statistics for Benzo(b)&(k)&(j)fluoranthene (ng/m³) for All Monitoring Sites (1994 – 1997)

City	Address	No. of Samples	% Detect	Mean DL	10th Perc.	90th Perc.	Max.	Mean	Standard Deviation	Median
Charlottetown	56 Fitzroy St.	6	100%	-	0.07	0.13	0.13	0.10	0.02	0.09
Halifax	1657 Barrington St.	6	100%	-	0.02	0.28	0.28	0.12	0.10	0.10
Kejimkujik		66	46%	0.02	0.00	0.19	1.37	0.08	0.19	0.01
St. Andrews		47	66%	0.01	0.01	0.28	0.82	0.13	0.20	0.05
Saint John	Forest Hills	5	100%	-	0.38	1.01	1.01	0.68	0.30	0.65
Jonquiere	Powell/Hoopes	87	99%	0.03	1.36	333.77	1048.79	103.99	199.22	13.04
Montreal	1125 Ontario	98	100%	-	0.33	6.34	47.54	2.85	5.28	1.53
Pt. Petre		31	90%	0.01	0.01	0.26	2.61	0.27	0.60	0.09
Toronto	Junction Triangle	89	93%	0.01	0.08	1.65	3.65	0.74	0.69	0.53
Hamilton	Elgin/Kelly	95	96%	0.02	0.27	12.07	21.74	3.40	4.75	1.15
Simcoe	Experimental Farm	29	97%	0.02	0.04	0.54	0.65	0.19	0.18	0.13
Windsor	University Ave.	37	100%	-	0.43	3.14	6.51	1.29	1.28	0.86
Windsor	College/Prince	92	100%	-	0.26	2.16	8.50	1.16	1.34	0.82
Walpole		16	100%	-	0.05	0.45	1.20	0.23	0.29	0.16
Winnipeg	65 Ellen St.	68	96%	0.02	0.07	0.71	47.80	1.08	5.77	0.28
Winnipeg	301 Weston St.	5	100%	-	0.21	1.09	1.09	0.48	0.35	0.36
Prince Albert		6	100%	-	0.02	0.36	0.36	0.15	0.13	0.11
Estevan		14	64%	0.02	0.01	0.30	0.92	0.15	0.24	0.07
Regina	Longman Cresc.	8	100%	-	0.01	0.16	0.16	0.08	0.05	0.08
Lloydminster	5021-49 St.	4	75%	0.02	0.01	0.93	0.93	0.32	0.42	0.22
Gray		9	22%	0.02	0.01	0.08	0.08	0.02	0.02	0.01
Edmonton	17th St/105th Ave.	75	99%	0.02	0.07	0.85	3.69	0.40	0.60	0.20
Edmonton	10255-104th St.	4	75%	0.01	0.01	0.17	0.17	0.09	0.06	0.09
Fort Saskatchewan	9209A-96 Ave.	5	100%	-	0.10	1.68	1.68	0.71	0.81	0.17
Fort McMurray		5	80%	0.02	0.01	0.18	0.18	0.09	0.07	0.05
Jasper Park	Snaring Warden Sta.	8	25%	0.01	0.00	0.44	0.44	0.06	0.15	0.00
Trail	Butler Park	5	100%	-	0.34	1.34	1.34	0.79	0.39	0.82
Whitehorse	Riverdale	5	100%	-	4.15	14.58	14.58	11.21	4.30	13.17
Vancouver	2550 W 10th Ave.	17	100%	-	0.15	2.13	3.31	0.74	0.84	0.37
Vancouver	Kensington Park	29	79%	0.02	0.00	0.42	0.89	0.20	0.22	0.15
Vancouver	Rocky Point Park	14	86%	0.03	0.01	2.04	2.29	0.60	0.71	0.41
Vancouver	Pitt Meadows	9	100%	-	0.02	1.10	1.10	0.31	0.34	0.19
Chilliwack	Airport	5	80%	0.03	0.01	0.09	0.09	0.04	0.03	0.02
Powell River	Henderson School	30	100%	-	0.05	1.29	1.93	0.40	0.55	0.14
Victoria	1250 Quadra St.	4	100%	-	0.20	3.78	3.78	1.11	1.77	0.27
All Sites		1,134	91%	0.02	0.02	4.15	1048.79	8.97	61.50	0.34

Table XIII: Summary Statistics for Indeno(1,2,3-cd)pyrene (ng/m³) for All Monitoring Sites (1994 – 1997)

City	Address	No. of Samples	% Detect	Mean DL	10th Perc.	90th Perc.	Max.	Mean	Standard Deviation	Median
Charlottetown	56 Fitzroy St.	6	100%	-	0.03	0.06	0.06	0.04	0.01	0.03
Halifax	1657 Barrington St.	6	100%	-	0.02	0.07	0.07	0.05	0.02	0.06
Kejimkujik		66	44%	0.02	0.00	0.07	0.21	0.02	0.03	0.01
St. Andrews		47	64%	0.01	0.01	0.09	0.28	0.04	0.06	0.02
Saint John	Forest Hills	5	100%	-	0.15	0.30	0.30	0.21	0.07	0.18
Jonquiere	Powell/Hoopes	87	99%	0.03	0.19	39.25	110.77	11.50	21.61	2.06
Montreal	1125 Ontario	98	99%	0.01	0.12	1.23	9.10	0.63	0.99	0.44
Pt. Petre		31	81%	0.01	0.00	0.09	0.51	0.07	0.11	0.03
Toronto	Junction Triangle	89	89%	0.01	0.01	0.61	1.41	0.29	0.29	0.19
Hamilton	Elgin/Kelly	95	96%	0.02	0.11	3.18	9.53	1.21	1.76	0.40
Simcoe	Experimental Farm	29	90%	0.02	0.01	0.14	0.17	0.05	0.05	0.04
Windsor	University Ave.	37	100%	-	0.13	1.28	2.03	0.48	0.43	0.34
Windsor	College/Prince	92	100%	-	0.11	0.78	2.24	0.41	0.41	0.27
Walpole		16	88%	0.01	0.01	0.16	0.51	0.07	0.12	0.04
Winnipeg	65 Ellen St.	68	93%	0.02	0.02	0.29	11.91	0.32	1.43	0.11
Winnipeg	301 Weston St.	5	100%	-	0.09	0.51	0.51	0.28	0.18	0.20
Prince Albert		6	83%	0.03	0.02	0.16	0.16	0.08	0.06	0.06
Estevan		14	64%	0.02	0.01	0.18	0.46	0.09	0.12	0.04
Regina	Longman Cresc.	8	100%	-	0.01	0.07	0.07	0.05	0.02	0.06
Lloydminster	5021-49 St.	4	75%	0.02	0.01	0.76	0.76	0.24	0.35	0.10
Gray		9	0%	0.02	0.01	0.01	0.01	0.01	0.00	0.01
Edmonton	17th St/105th Ave.	75	95%	0.02	0.03	0.45	1.65	0.19	0.27	0.09
Edmonton	10255-104th St.	4	75%	0.02	0.01	0.09	0.09	0.04	0.04	0.03
Fort Saskatchewan	9209A-96 Ave.	5	100%		0.04	0.85	0.85	0.35	0.41	0.09
Fort McMurray		5	60%	0.03	0.01	0.10	0.10	0.04	0.04	0.02
Jasper Park	Snaring Warden Sta.	8	38%	0.01	0.00	0.35	0.35	0.05	0.12	0.01
Trail	Butler Park	5	100%	-	0.21	0.56	0.56	0.34	0.14	0.33
Whitehorse	Riverdale	5	100%	-	1.28	9.66	9.66	6.34	3.49	6.90
Vancouver	2550 W 10th Ave.	17	100%	-	0.06	0.74	1.38	0.31	0.35	0.15
Vancouver	Kensington Park	29	93%	0.03	0.02	0.35	0.38	0.10	0.12	0.06
Vancouver	Rocky Point Park	14	71%	0.03	0.01	0.85	1.08	0.25	0.32	0.15
Vancouver	Pitt Meadows	9	89%	0.01	0.01	0.55	0.55	0.15	0.19	0.08
Chilliwack	Airport	5	100%	-	0.01	0.05	0.05	0.02	0.02	0.01
Powell River	Henderson School	30	97%	0.01	0.02	0.45	0.50	0.11	0.13	0.06
Victoria	1250 Quadra St.	4	100%	-	0.09	1.70	1.70	0.51	0.79	0.15
All Sites		1134	88%	0.02	0.01	1.16	110.77	1.21	6.71	0.13

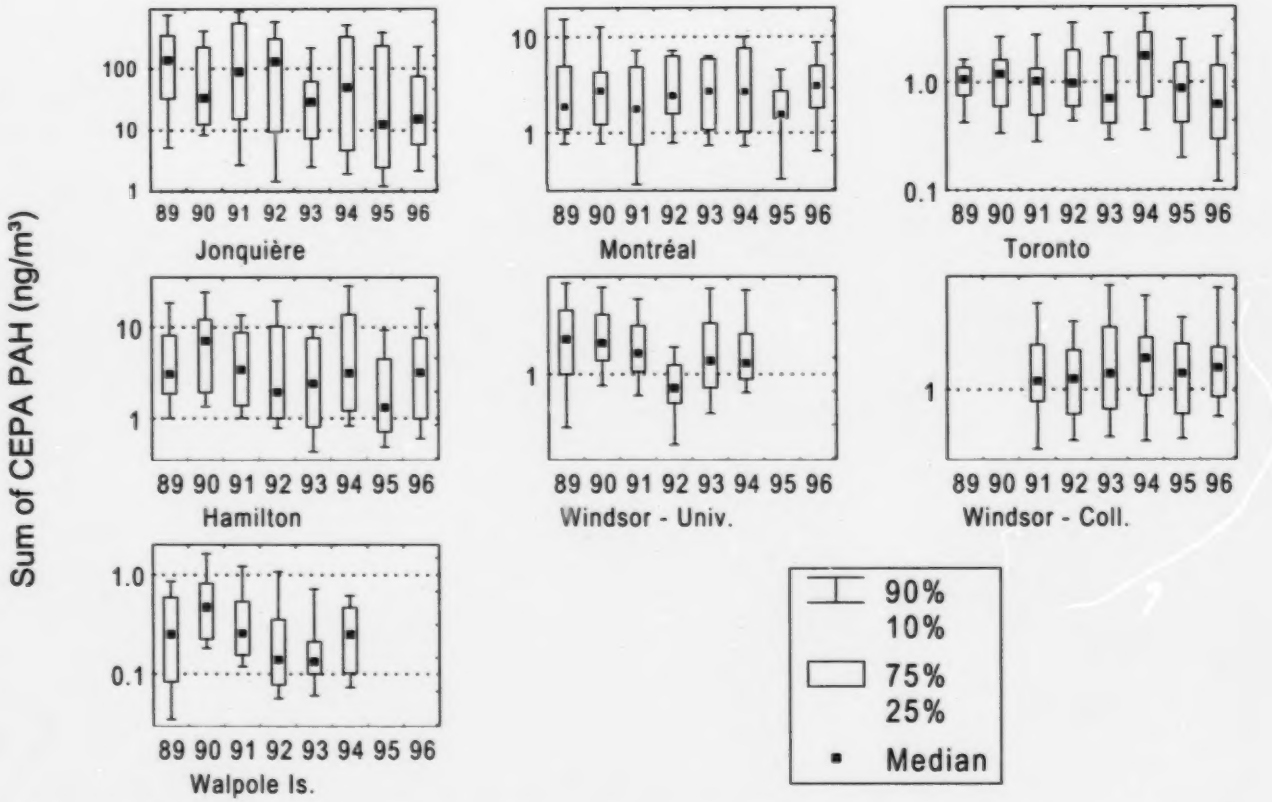


Figure 6: Yearly Variation and Trend in Sum of CEPA Toxic (Health) PAH (benzo(a)pyrene, benzo(b)&(k)&(j)fluoranthene and indeno(1,2,3-cd)pyrene for Sites With Longest Data Record (1989 – 1996).

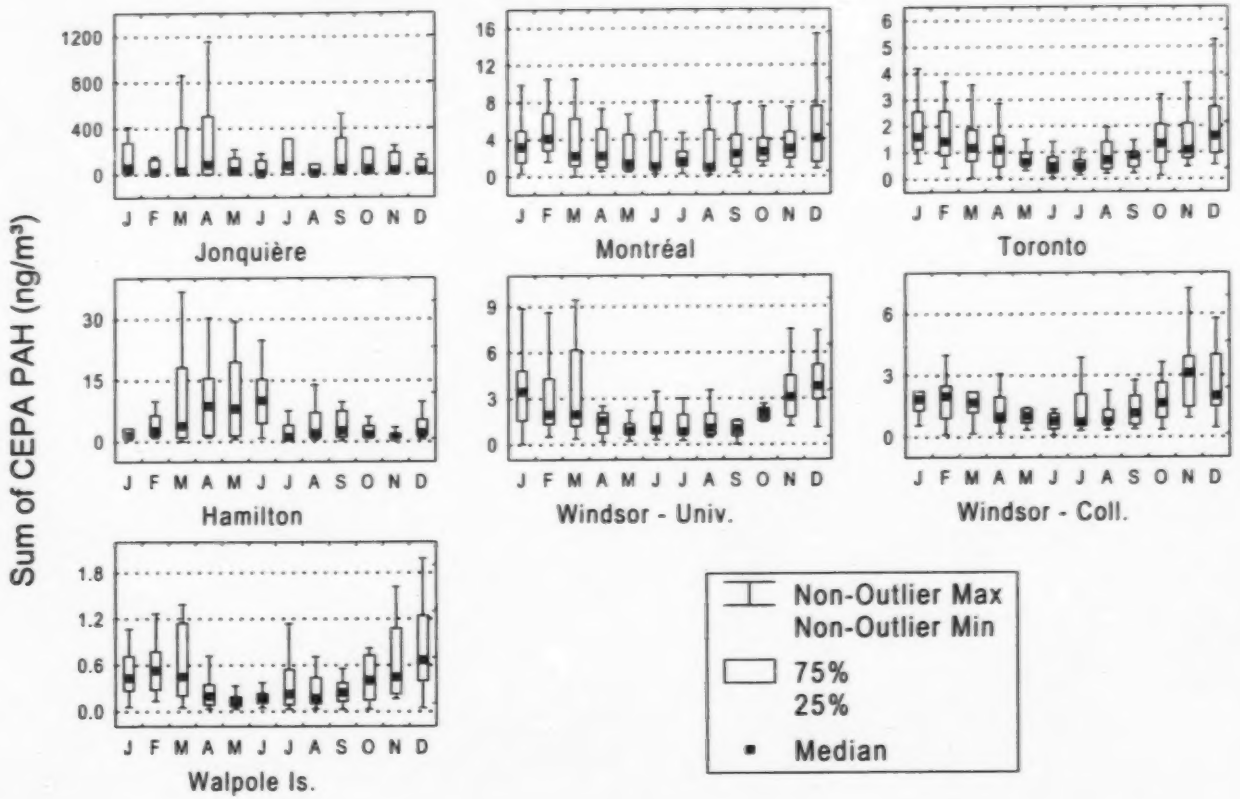


Figure 7: Monthly Variation in Sum of CEPA Toxic (Health) PAH (benzo(a)pyrene, benzo(b)&(k)&(j)fluoranthene and indeno(1,2,3-cd)pyrene for Sites With Longest Data Record (1989 – 1996).

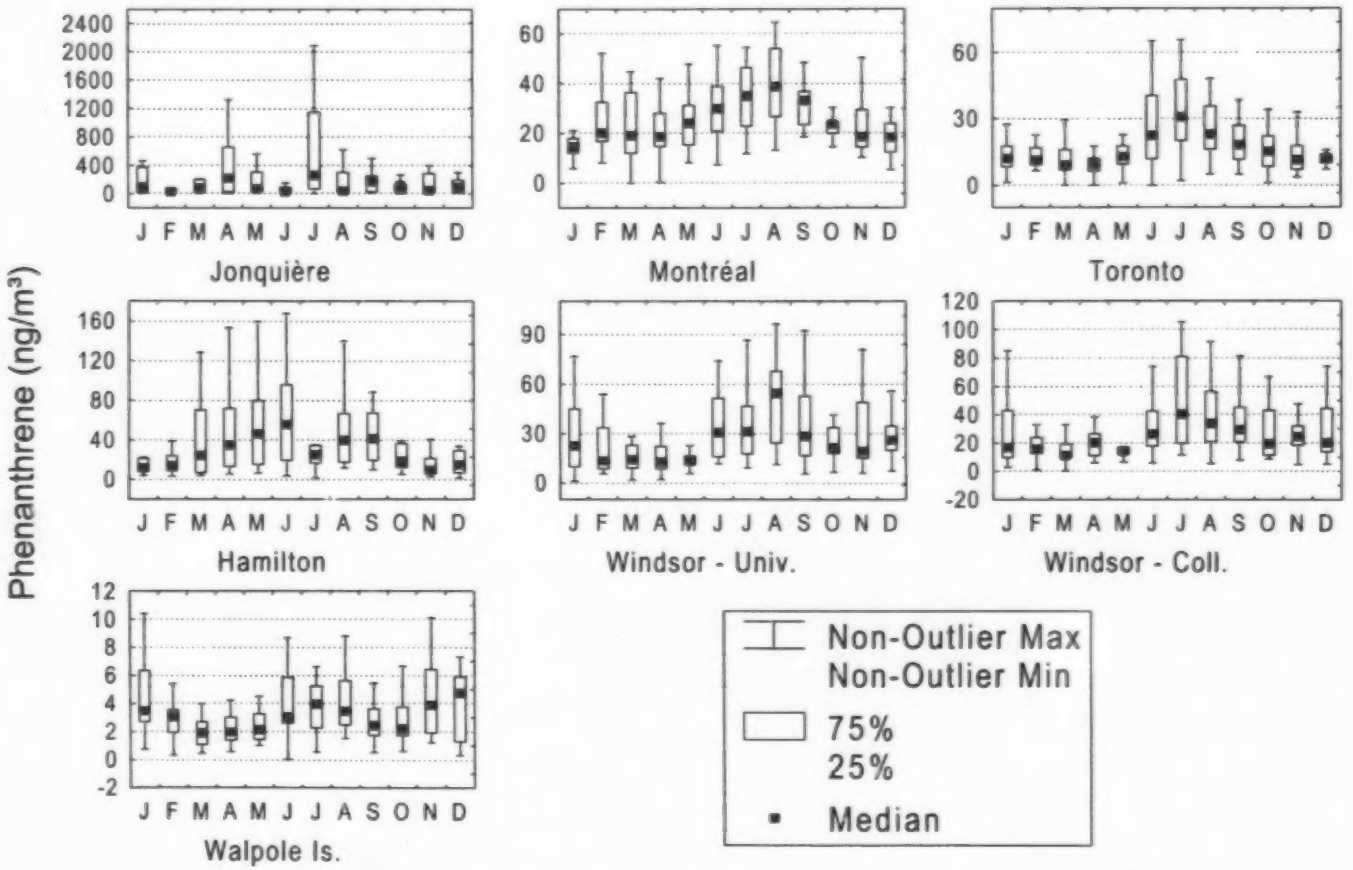


Figure 8: Monthly Variation in Phenanthrene for Sites with Longest Data Record (1989 – 1996)

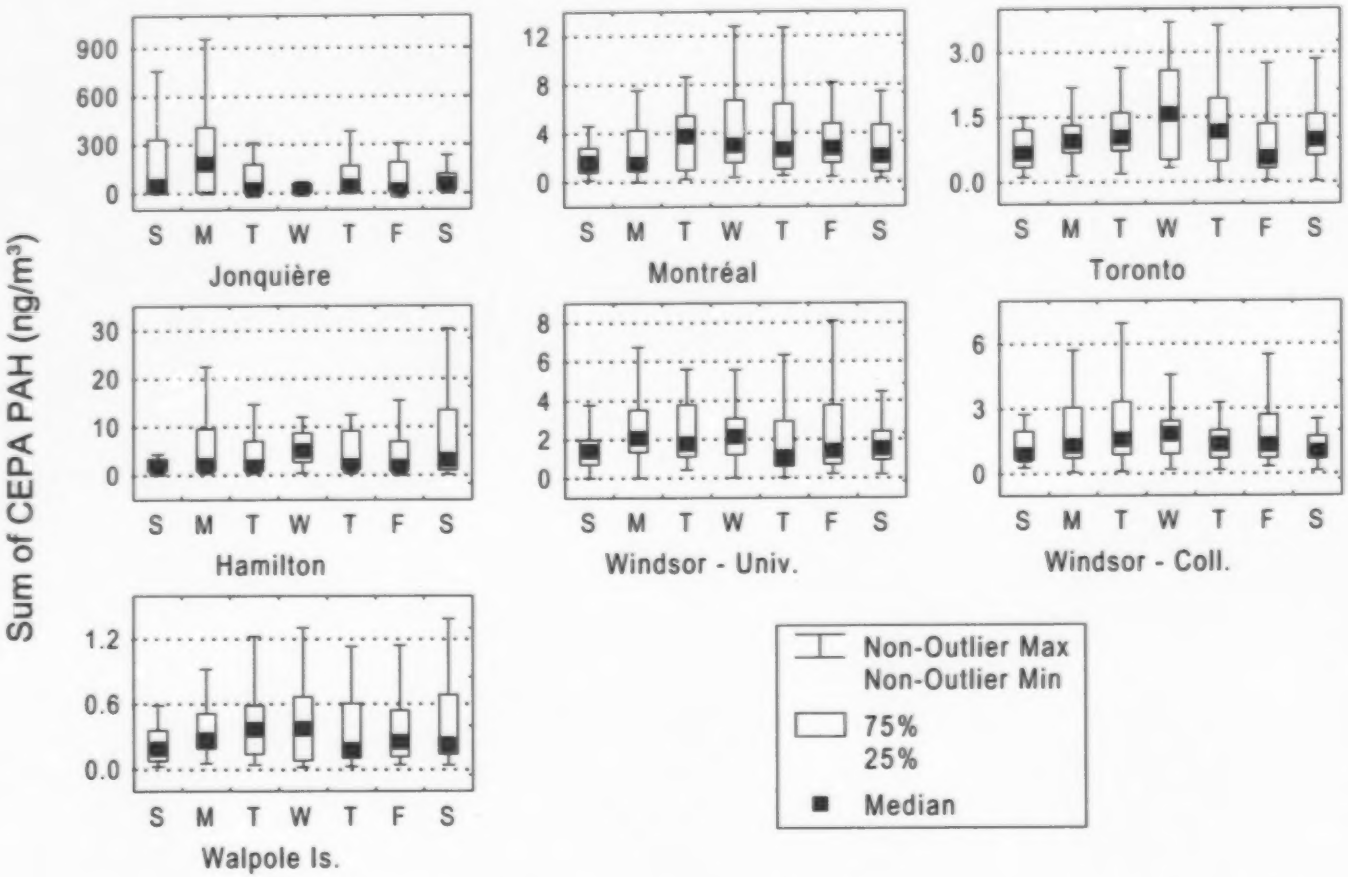


Figure 9: Day of Week Variation in Sum of CEPA Toxic (Health) PAH (benzo(a)pyrene, benzo(b)&(k)&(j)fluoranthene and indeno(1,2,3-cd)pyrene for Sites With Longest Data Record (1989 – 1997).

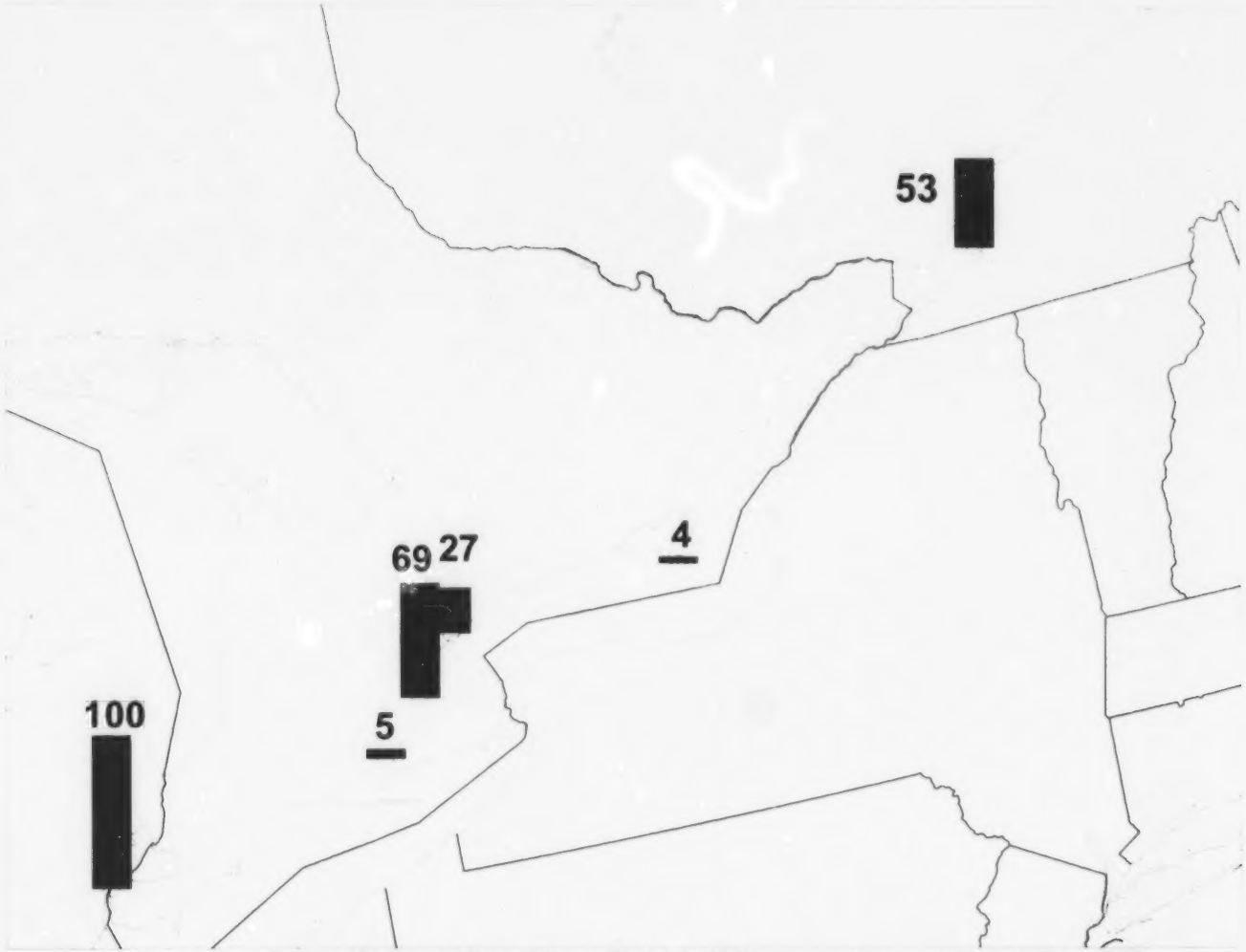


Figure 10: Spatial Variability of Total PAH Concentrations (ng/m³) for 1996 – 1997
(For 24 sampling days with simultaneous observations)

Ambient Air PCDD/PCDF Concentrations

Over 500 daily samples were collected for PCDD/PCDF analysis from 34 monitoring sites with 344 samples collected between 1994 and 1997. For many sites, however, only 2 or 3 days of data are available. The only sites with long data records are Windsor-University Ave. (1989 to 1995), Windsor-College and Prince (1990-1997) and Walpole Island (1989-1995). *Figure 11* shows mean, 10^{th} and 90^{th} percentile TEQ concentrations for all sites organized by site type (1994 to 1997 data). The TEQ concentrations were computed by multiplying each 2,3,7,8-substituted PCDD and PCDF isomer concentration by its TEF value and summing the results. The graph shows results for two separate ways of handling values below detection. In the first case, one-half the detection level was substituted for values below detection before multiplying by the TEF. In the second case, zero is substituted for values below detection. Because of the low detection levels achieved in the study, the method of handling non-detects really only impacts results for the cleanest sites. In the Figure, the sites are grouped by site category. Since specific source emission estimates are not available, the assignment of sites to the source impact category is somewhat arbitrary although it is clear that these sites record much higher TEQ concentrations than 'typical' urban sites. Overall, mean TEQ concentrations (using 0.5-DL substitution) ranged from 105 fg/m^3 at the Toronto site to 10 fg/m^3 at St. Andrews, N.B. For sites with more than ten sampling days, 90^{th} percentile TEQ values ranged from 326 fg/m^3 at the Jonquière site to 16 fg/m^3 at Kejimkujik.

Table XIV provides summary statistics and frequency of detection for all 2,3,7,8 isomers and for total congener class results using all data for all sites. As shown in the table octa-PCDD is the most abundant isomer and was detected in all samples (it was also detected in all field blanks with measured levels generally less than 60 fg/m^3 at urban sites and less than 20 fg/m^3 at rural sites), followed by hepta-PCDD and hepta and octa-PCDF. Maximum concentrations of 73 pg/m^3 of total PCDD, 37 pg/m^3 of total PCDF and 1.95 pg/m^3 TEQ were recorded during the program. The isomer 2,3,7,8-T_4CDD was detected in 28% of the samples with a median concentration of 3 fg/m^3 and a maximum of 61 fg/m^3. The contribution of the PCDD and PCDF isomers to computed TEQ is summarized in *Figure 12* (using TEFs of Table V). The relative abundance of the isomers (excluding octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzofuran (OCDF) is shown in *Figure 13* and the relative abundance of the congener class sums is provided in *Figure 14*. Although the octa and hepta congeners are most abundant they are also the least toxic and make only a small contribution to TEQ. Four isomers, 2,3,4,7,8-P_5CDF, 2,3,7,8-T_4CDF, 1,2,3,7,8-P_5CDD and 1,2,3,4,7,8-H_6CDF, account for 65% of computed TEQ. Because the three furan isomers alone contribute 54% of TEQ, total PCDF is highly correlated with computed TEQ as shown in *Figure 15*. The urban and rural mean profiles in *Figures 13 and 14* are similar, with the rural distributions enhanced in hepta and octa-PCDD. The rural samples had generally non-detectable levels of the 2,3,7,8-substituted tetra through hexa-PCDD but similar fractions of tetra and hepta-PCDF to the urban sites. The more rapid rate of removal of tetra through hexa-PCDD and PCDF from the atmosphere as compared to hepta and octa-PCDD and PCDF is responsible for the change in relative abundance of isomers and congener classes when distance to source regions increase[21]. The estimated half-life for 2,3,7,8-T_4CDD due to photolysis is 1.6 days vs. 10 days for OCDD[16]. *Figure 16* compares the urban average isomer profile for days in Toronto, and Windsor with TEQ over 100 fg/m^3 (5 sampling days in Toronto and 23 at the Windsor site in the 1989-94 time period). For these high concentration days, the relative abundance of isomers is similar to the urban average with

enhanced levels of three hexa-PCDF isomers and especially of 1,2,3,4,7,8-H_6CDF. As discussed in previous reports, a municipal incinerator in Detroit impacted the Windsor site. The most abundant isomers in the incinerator stack emission were 2,3,7,8-T_4CDF, 1,2,3,4,7,8-H_6CDF and 1,2,3,4,6,7,8-H_7CDF.

Summary statistics by site are provided for 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-T_4CDF) and 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-P_5CDF) in *Tables XV* and *XVI.* Mean concentrations of 2,3,7,8-T_4CDF ranged from 5 to 188 fg/m^3 with 90th percentile values ranging from 10 to 574 fg/m^3. The isomer was detected in 93% of the samples. The 2,3,4,7,8-P_5CDF isomer was detected in 76% of samples with site mean concentrations ranging from 5 to 53 fg/m^3 and 90th percentile values ranging from 5 to 192 fg/m^3.

Only three sites have a complete multi-year record of PCDD/PCDF measurements. Yearly variations and trends in TEQ and total PCDF at the two Windsor sites and the Walpole Island site are shown in *Figures 17 and 18.* As discussed in previous reports[3,4] concentrations of PCDD/PCDF have declined at these sites due to installation of best available control technology on the Detroit incinerator.

Figure 19 provides an indication of spatial variability of TEQ concentrations from urban to rural sites between Windsor and Montréal. The bars represent average concentrations per site using data from 10 sampling days in 1996 and 1997 when all sites were operational. The urban site mean concentrations ranged from a factor of 2 to 8 times higher than nearby rural sites.

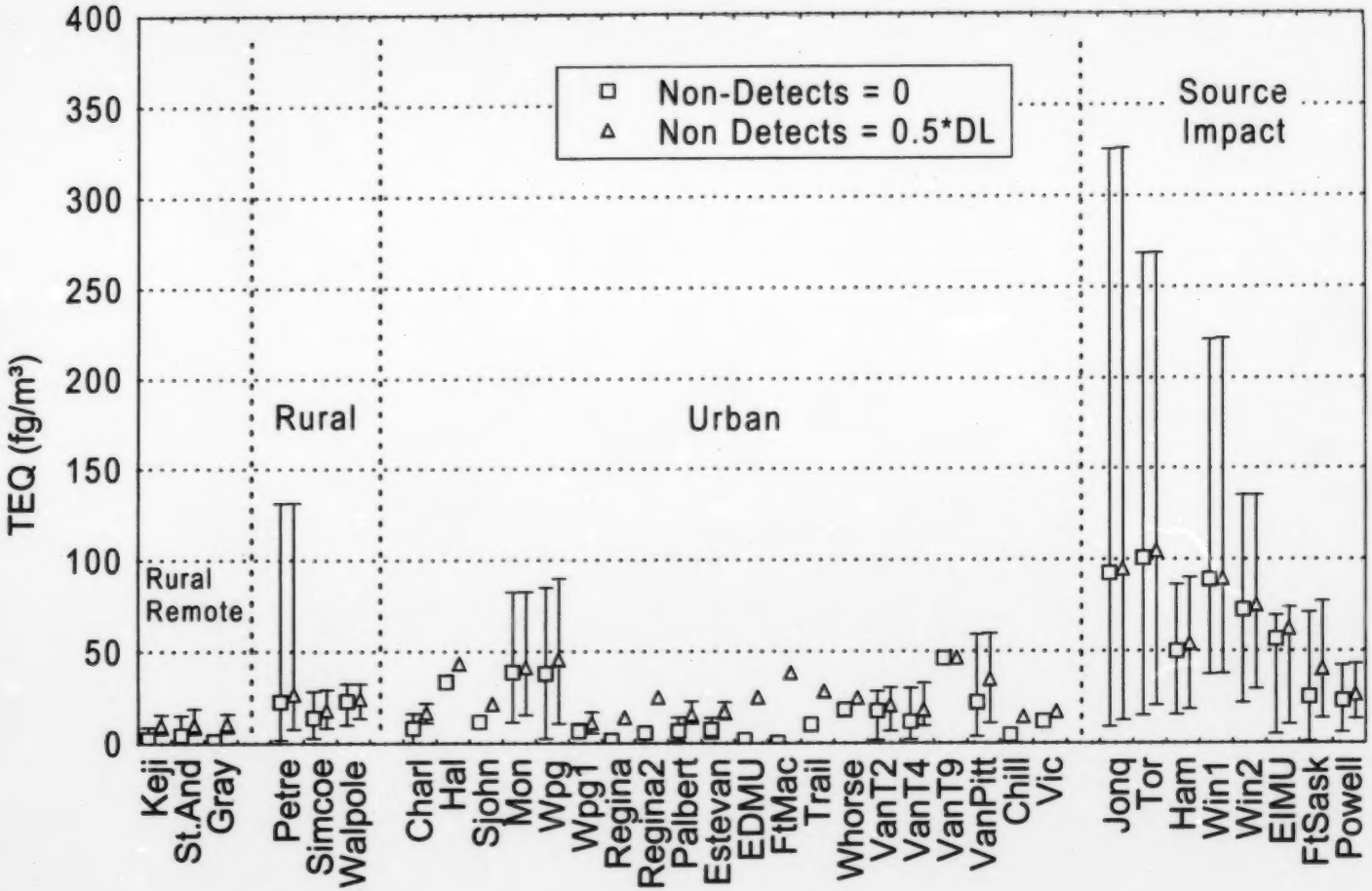


Figure 11: Mean, 10th and 90th Percentile TEQ Concentrations (fg/m³) by Site (1994-1997)

Table XIV: Overall Summary Statistics (fg/m³) and Frequency of Detection for all PCDD and PCDF Isomers and Congener Classes (1989 to 1997)

Isomer/Congener	Number of Sampling Days	Frequency of Detection	Mean	Standard Deviation	Median	Maximum	Minimum
2,3,7,8-T_4CDD	526	28%	5	7	3	61	0.2
1,2,3,7,8-P_5CDD	526	55%	14	23	7	220	0.4
1,2,3,4,7,8-H_6CDD	526	51%	15	24	8	293	0.4
1,2,3,6,7,8-H_6CDD	526	69%	29	58	15	816	0.9
1,2,3,7,8,9-H_6CDD	526	67%	38	73	18	958	0.4
1,2,3,4,6,7,8-H_7CDD	526	98%	272	401	166	4,436	4.5
2,3,7,8-T_4CDF	526	95%	104	222	49	4,108	1.3
1,2,3,7,8-P_5CDF	526	67%	27	63	9	754	0.5
2,3,4,7,8-P_5CDF	526	77%	42	134	14	2,621	0.5
1,2,3,4,7,8-H_6CDF	526	76%	79	179	24	1,718	0.6
1,2,3,6,7,8-H_6CDF	526	74%	38	89	13	917	0.5
2,3,4,6,7,8-H_6CDF	526	71%	44	107	15	1,309	0.5
1,2,3,7,8,9-H_6CDF	526	19%	9	44	3	839	0.4
1,2,3,4,6,7,8-H_7CDF	526	92%	153	354	60	4,338	1.2
1,2,3,4,7,8,9-H_7CDF	526	55%	27	114	9	2,116	0.7
T_4CDD	526	75%	115	219	36	1,991	0.2
P_5CDD	526	75%	161	335	50	2,860	0.4
H_6CDD	526	88%	342	656	165	8,017	1.5
H_7CDD	526	98%	579	868	364	11,304	5.9
O_8CDD	526	100%	873	3192	496	70,970	8.0
TOTAL PCDD	526	100%	2047	4025	1202	73,106	8.0
T_4CDF	526	95%	560	1101	254	18,266	1.4
P_5CDF	526	92%	428	953	143	12,193	1.0
H_6CDF	526	90%	371	823	127	7,454	0.5
H_7CDF	526	92%	276	740	104	11,695	1.2
O_8CDF	526	85%	150	664	50	12,816	0.1
TOTAL PCDF	526	100%	1743	3565	695	37,193	1.4
TEQ	526	100%	75	141	36	1,950	3.9

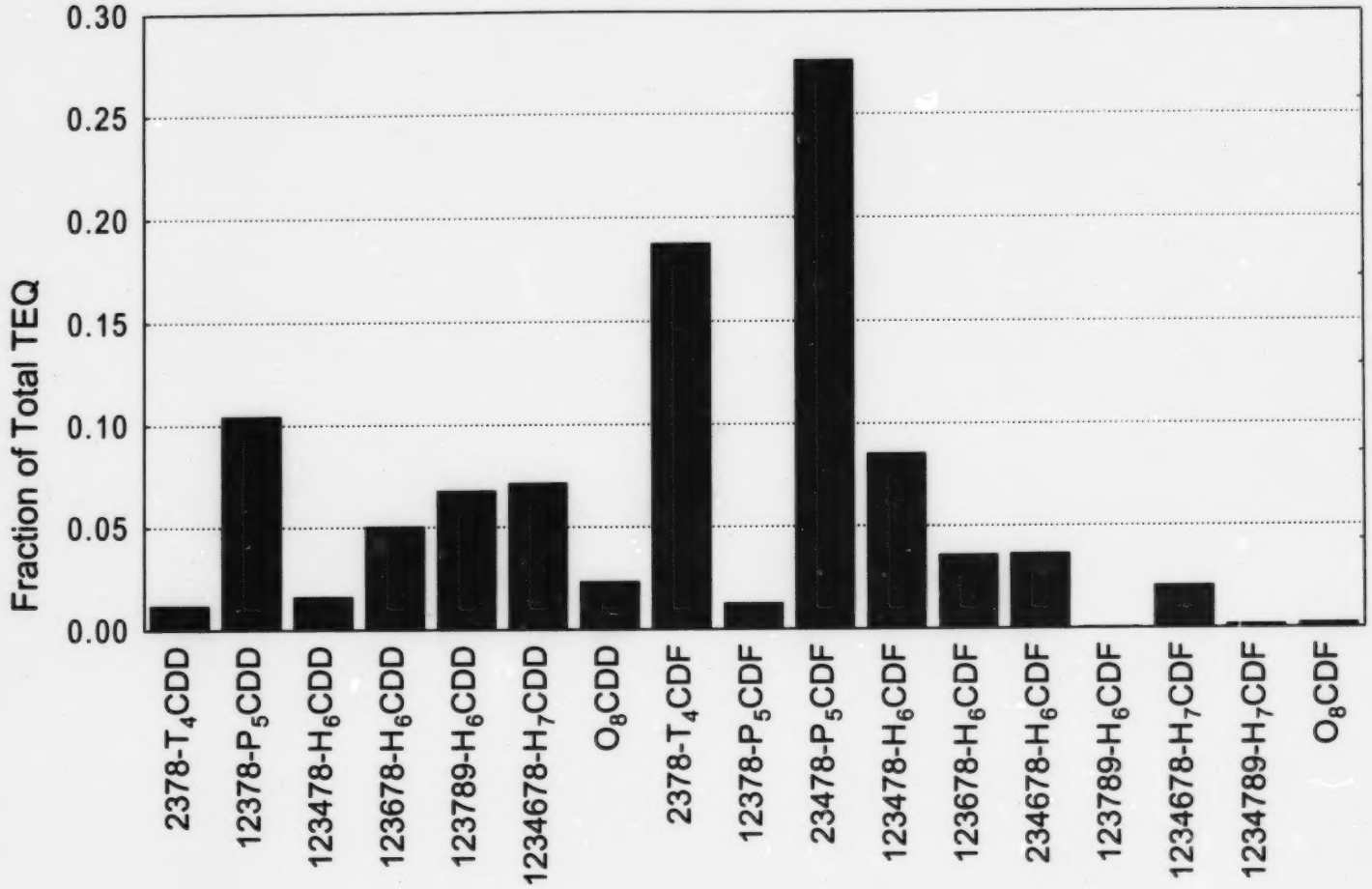


Figure 12: Relative Contribution of 2,3,7,8 Isomers to TEQ for All Sites (1994 to 1997).

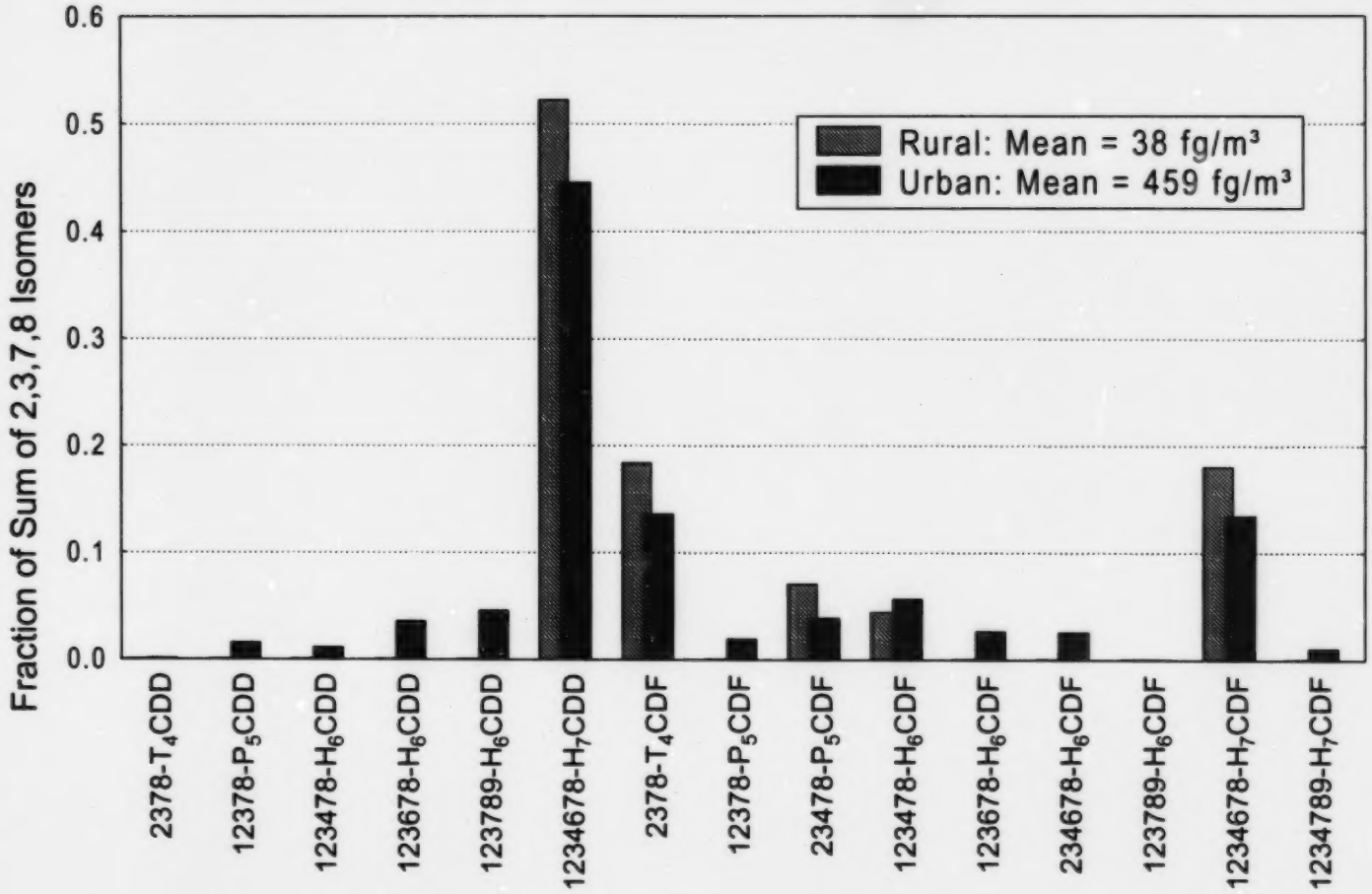


Figure 13: Distribution of 2,3,7,8 Substituted Isomers (Octa-PCDD and Octa-PCDF excluded) for Rural and Urban Sites (1994 to 1997)

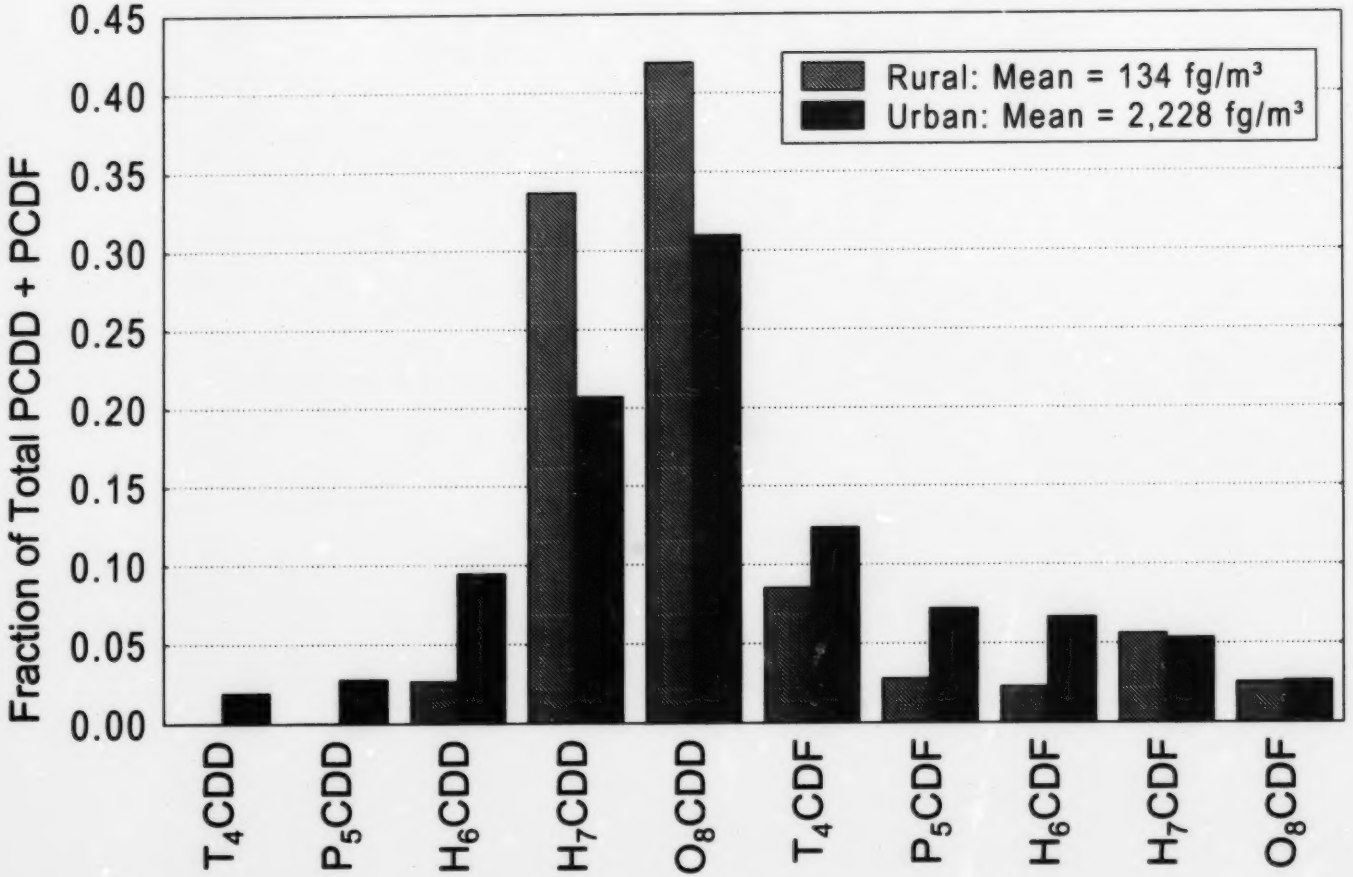
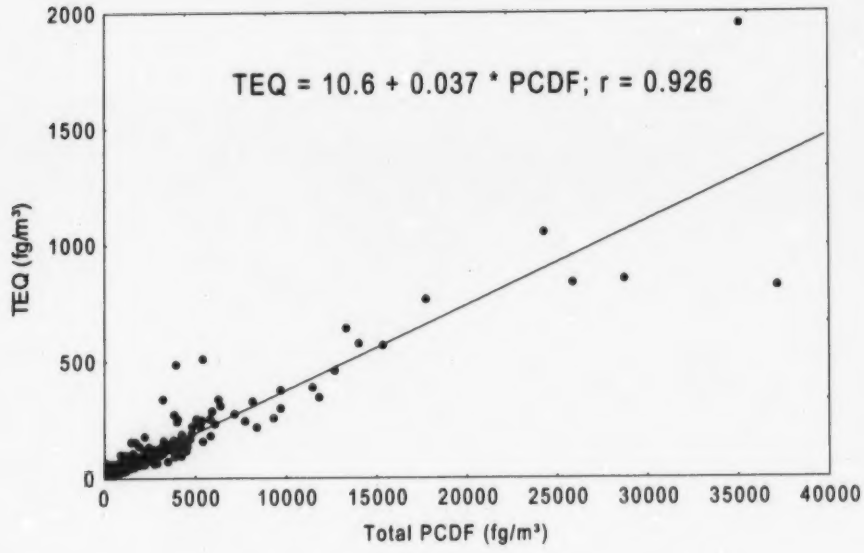


Figure 14: Distribution of PCDD and PCDF by Congener Class for Urban and Rural Sites (1994 to 1997)



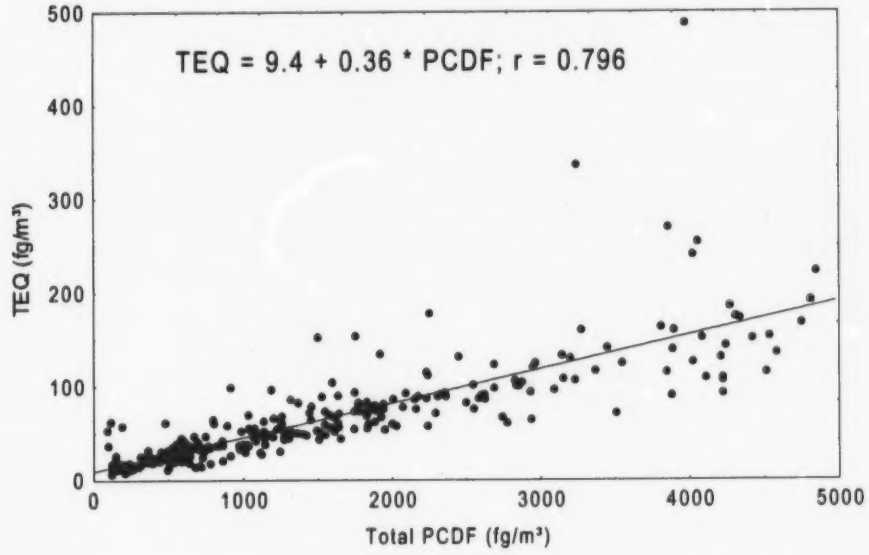


Figure15: Relationship Between TEQ and Total PCDF Using All Data from All Sites

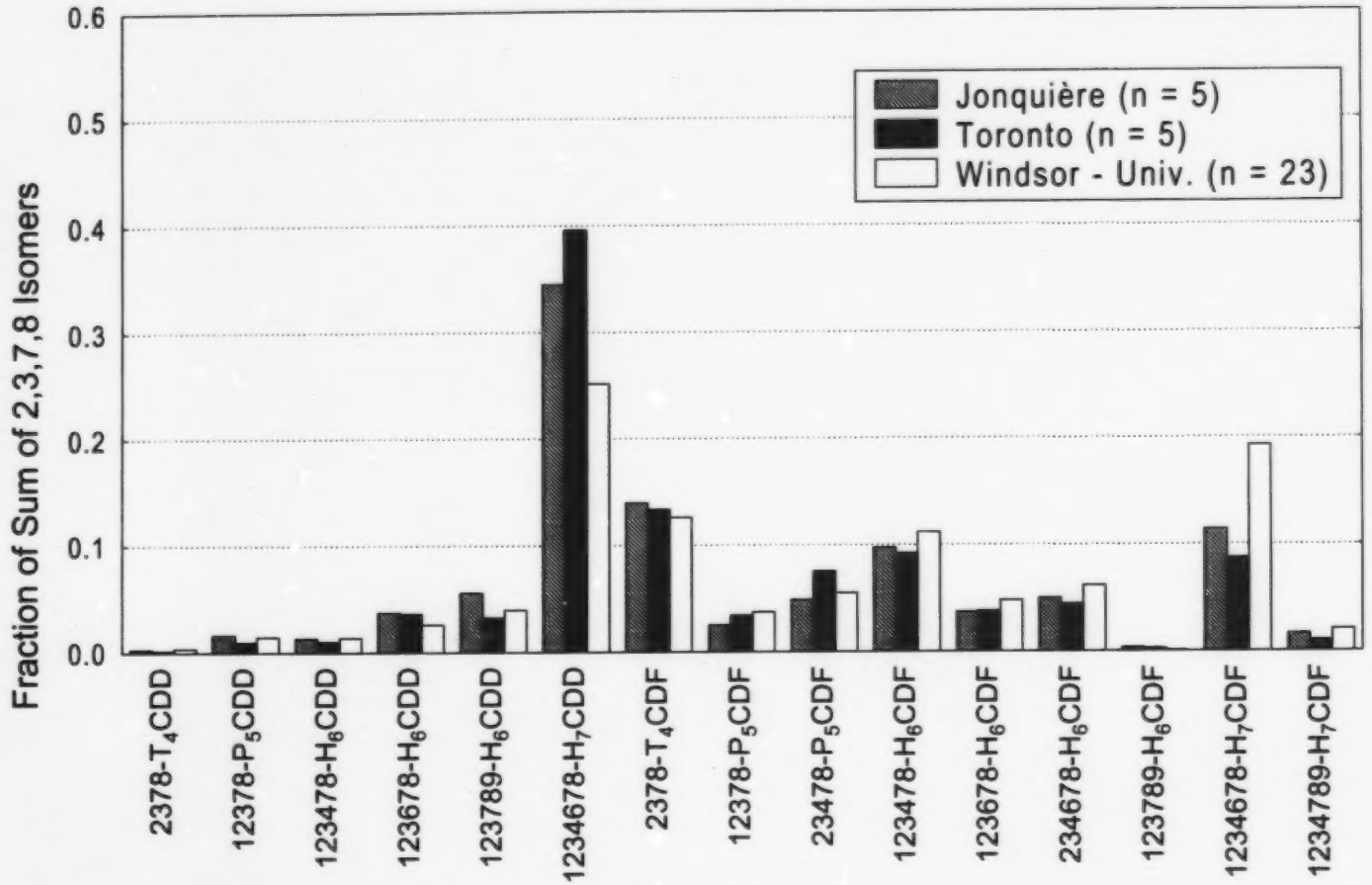


Figure 16: Distribution of 2,3,7,8 Substituted Isomers (Octa-PCDD and Octa-PCDF excluded) for Sampling Days with TEQ Values > 100 fg/m³ - Jonquière, Toronto and Windsor

Table XV: Summary Statistics for 2,3,7,8-TCDF (fg/m³) for All Monitoring Sites (1994 – 1997)

City	Address	No. of Samples	% Detect	10th Perc.	90th Perc.	Max.	Mean	Standard Deviation	Median
Charlottetown	56 Fitzroy St.	3	67%	6.7	48.8	48.8	30.1	21.4	34.7
Halifax	1657 Barrington St.	2	100%	-	-	230.3	126.9	-	-
Kejimkujik National Park		19	53%	2.0	10.0	13.1	5.2	3.2	4.8
St. Andrews		19	74%	2.0	11.5	24.0	6.8	5.1	4.9
Saint John	Forest Hills	2	100%	-	-	29.8	22.8	-	-
Jonquière	Powell/Hoopes	15	100%	19.2	573.9	1056.0	187.8	278.6	85.5
Montréal	1125 Ontario	23	100%	22.4	107.8	174.2	55.7	42.4	44.2
Point Petre		10	100%	3.5	230.6	230.6	35.5	69.3	16.4
Toronto	Junction Triangle	24	100%	30.4	237.2	839.7	133.7	184.9	76.0
Hamilton	Elgin/Kelly	28	100%	21.4	153.1	294.0	84.2	60.9	83.2
Simcoe	Experimental Farm	11	100%	7.3	29.9	32.7	18.6	9.6	20.6
Windsor	University Ave.	20	100%	91.8	347.1	347.7	169.9	82.5	154.4
Windsor	College/Prince	41	100%	41.5	223.1	512.6	132.9	94.5	113.9
Walpole		13	92%	8.7	63.5	100.6	34.7	27.0	24.7
Winnipeg	65 Ellen St.	26	96%	11.7	76.4	187.6	37.2	41.3	21.7
Winnipeg	301 Weston St.	3	100%	15.0	45.7	45.7	30.1	15.3	29.7
Regina	Longman Cresc.	2	100%	-	-	7.8	7.6	-	-
Regina	2505 11th St.	2	100%	-	-	40.6	28.9	-	-
Prince Albert		5	100%	7.5	19.0	19.0	11.7	4.6	11.7
Estevan		3	100%	8.6	11.5	11.5	9.8	1.5	9.3
Gray		4	50%	1.9	6.1	6.1	4.0	1.7	4.0
Edmonton	17th St. & 105th Ave.	21	100%	4.9	121.7	608.7	72.4	163.5	17.4
Edmonton	10255 104th St.	2	50%	-	-	15.7	10.7	-	-
Fort Saskatchewan	9209A-96 Ave.	5	60%	2.5	130.1	130.1	46.7	57.1	13.5
Fort McMurray		2	0%	-	-	12.8	12.7	-	-
Trail	Butler Park	2	100%	-	-	75.3	74.0	-	-
Whitehorse	Riverdale	2	100%	-	-	95.3	91.1	-	-
Vancouver	Kitsilano	3	100%	8.3	29.7	29.7	20.4	10.9	23.2
Vancouver	Kensington Park	12	100%	10.6	32.5	40.7	17.6	9.9	14.1
Vancouver	Rocky Point Park	1	100%	-	-	41.3	41.3	-	-
Vancouver	Pitt Meadows	4	100%	27.0	84.7	84.7	57.3	24.3	66.0
Chilliwack	Airport	2	100%	-	-	45.9	32.9	-	-
Powell River	Henderson School	12	100%	19.0	110.0	151.8	51.8	39.6	42.0
Victoria	1250 Quadra St.	1	100%	-	-	46.0	46.0	-	-
All Sites		344	93%	5.9	172.5	1056.0	72.0	111.3	32.7

Table XVI: Summary Statistics for 2,3,4,7,8-P_5CDF (fg/m³) for All Monitoring Sites (1994 – 1997)

City	Address	No. of Samples	% Detect	10th Perc.	90th Perc.	Max.	Mean	Standard Deviation	Median
Charlottetown	56 Fitzroy St.	3	33%	1.2	5.0	5.0	3.7	2.2	4.9
Halifax	1657 Barrington St.	2	50%	-	-	35.1	18.1	-	-
Kejimkujik National Park		19	26%	1.0	17.0	17.5	4.9	5.2	3.0
St. Andrews		19	58%	1.8	11.9	17.0	4.7	4.3	2.4
Saint John	Forest Hills	2	50%	-	-	11.1	7.3	-	-
Jonquiere	Powell/Hoopes	15	93%	2.3	192.3	270.7	49.5	78.0	18.1
Montreal	1125 Ontario	23	96%	5.2	31.6	37.6	15.9	10.3	12.2
Point Petre		10	70%	1.4	78.4	78.4	15.2	23.1	8.4
Toronto	Junction Triangle	24	96%	8.8	143.1	325.4	52.9	85.3	17.0
Hamilton	Elgin/Kelly	28	96%	7.5	55.1	105.0	28.0	23.8	23.9
Simcoe	Experimental Farm	11	73%	2.0	12.9	13.1	6.6	4.3	4.7
Windsor	University Ave.	20	95%	9.7	103.9	122.1	39.6	32.1	31.2
Windsor	College/Prince	41	95%	8.9	69.7	152.3	37.3	31.2	28.4
Walpole		13	92%	4.4	14.8	26.8	10.1	6.2	8.9
Winnipeg	65 Ellen St.	26	65%	1.8	25.6	59.3	12.6	12.2	9.8
Winnipeg	301 Weston St.	3	67%	1.0	6.0	6.0	3.1	2.6	2.3
Regina	Longman Cresc.	2	0%	-	-	2.2	2.1	-	-
Regina	2505 11th St.	2	50%	-	-	10.1	8.6	-	-
Prince Albert		5	20%	2.5	3.3	3.3	2.8	0.3	2.7
Estevan		3	33%	3.0	8.2	8.2	5.1	2.7	4.0
Gray		4	25%	1.9	6.1	6.1	3.7	1.8	4.0
Edmonton	17th St. & 105th Ave.	21	62%	1.6	38.6	213.8	28.2	61.9	6.1
Edmonton	10255 104th St.	2	0%	-	-	7.5	6.6	-	-
Fort Saskatchewan	9209A-96 Ave.	5	40%	2.5	35.6	35.6	16.8	16.3	7.5
Fort McMurray		2	0%	-	-	12.5	11.4	-	-
Trail	Butler Park	2	50%	-	-	8.7	7.4	-	-
Whitehorse	Riverdale	2	100%	-	-	10.1	8.6	-	-
Vancouver	Kitsilano	3	67%	1.5	21.2	21.2	13.4	10.5	17.6
Vancouver	Kensington Park	12	33%	1.4	13.8	15.7	5.5	5.0	4.1
Vancouver	Rocky Point Park	1	100%	-	-	23.4	23.4	-	-
Vancouver	Pitt Meadows	4	50%	2.2	28.8	28.8	11.5	11.9	9.2
Chilliwack	Airport	2	0%	-	-	2.8	2.7	-	-
Powell River	Henderson School	12	83%	2.4	29.0	39.3	12.2	11.4	9.4
Victoria	1250 Quadra St.	1	100%	-	-	7.3	7.3	-	-
All Sites		344	73%	2.0	49.4	325.4	22.0	38.4	10.1

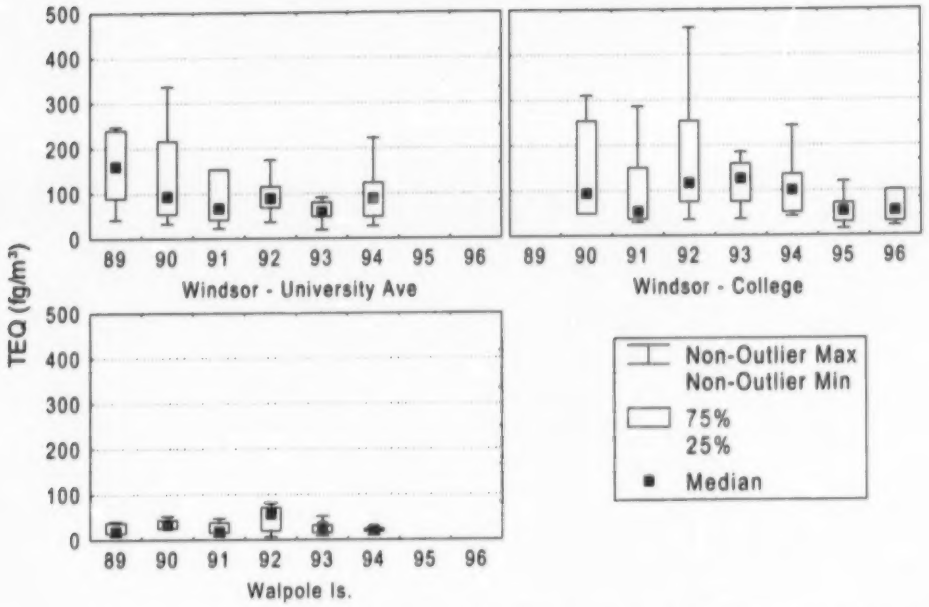


Figure 17: Annual Variation and Trend in TEQ at Windsor Area Sites (1989-1996)

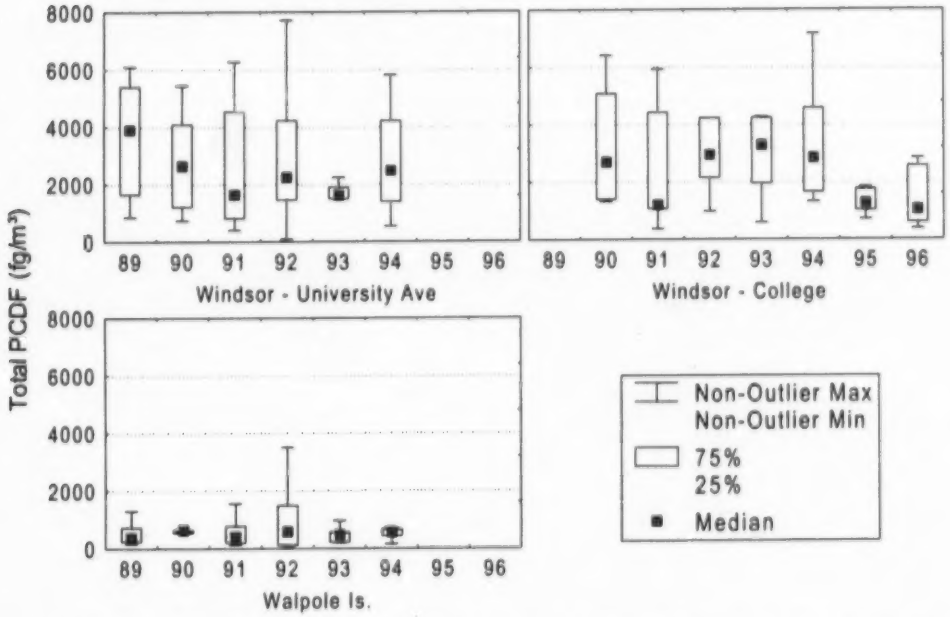


Figure18: Annual Variation and Trend in Total PCDF at Windsor Area Sites (1989-1996)

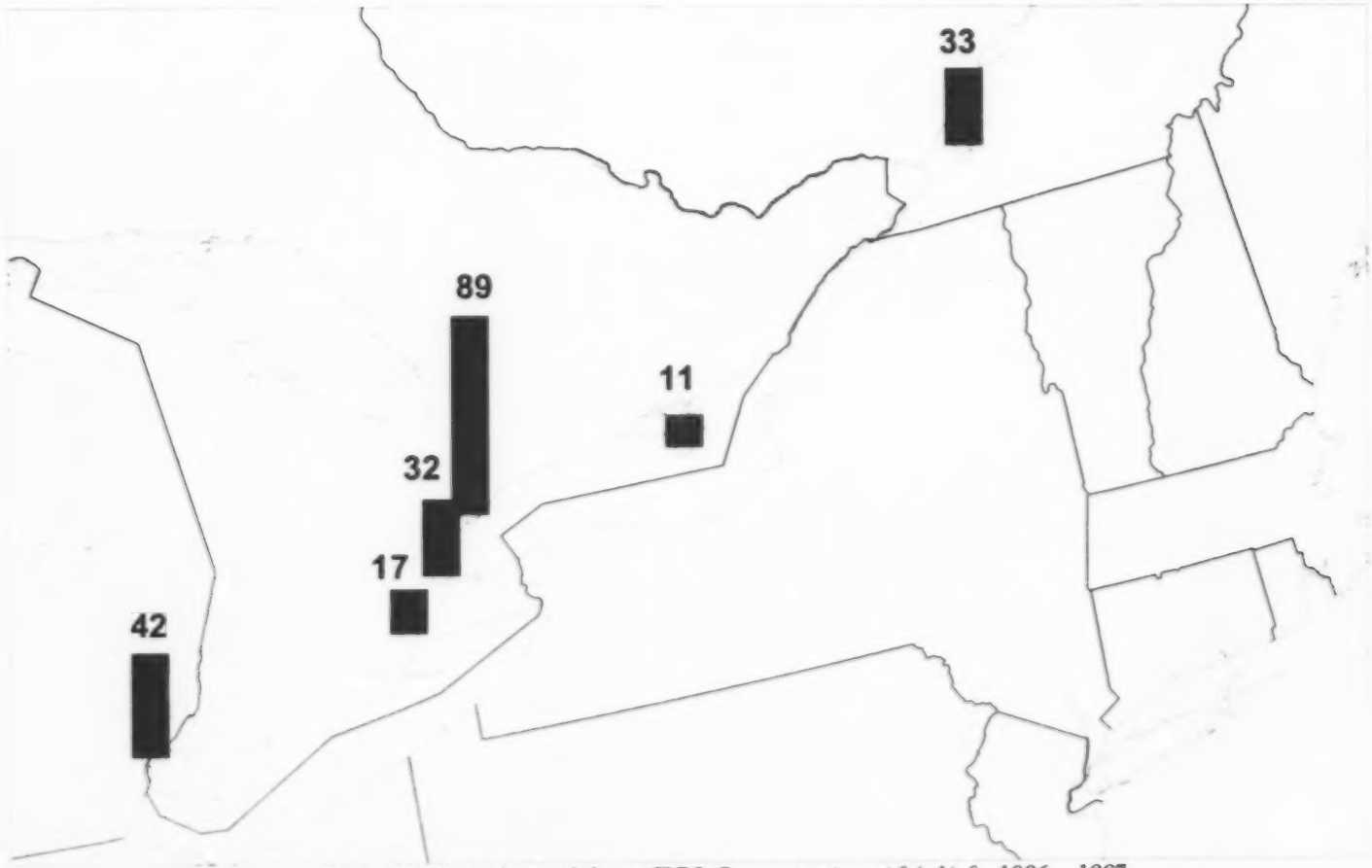


Figure19: Spatial variability of TEQ Concentrations (fg/m³) for 1996 – 1997
(For 10 sampling days with simultaneous observations)

Conclusions

Polycyclic aromatic hydrocarbons, polychlorinated dibenzo-*p*-dioxins and dibenzofurans are ubiquitous in air samples collected in rural and urban locations in Canada. Mean total PAH concentrations vary by almost three orders of magnitude between remote rural sites and source impacted urban locations while mean PCDD/PCDF concentrations (expressed as 2,3,7,8-T_4CDD toxic equivalents vary by a factor of 20. There is an even greater range in measured 90^{th} percentile concentrations. While there has been some apparent reductions in air concentrations over the past ten years, it is clear that there are still numerous sources of these toxic substances in Canada. These sources create both immediate and long range impacts. Additional efforts are required in characterizing and quantify emission releases of PAH and PCDD/PCDF and in determining the impact of specific sources on measurement sites. Because of the many known harmful effects of these classes of substance, it would be prudent to accelerate efforts to reduce environmental exposures.

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